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Zachary William Meduna

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EFFECTS OF TEMPERATURE AND FEEDSTOCK COMPOSITION ON PRODUCT DISTRIBUTION OF MIXED PLASTIC WASTE PYROLYSIS

by

Zachary William Meduna

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Abstract

Plastic is one of the most widely used packaging materials; however, there are limited processes in place for recycling at the end of its life, especially for plastics 3-7 including: PVC, low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS). Pyrolysis, or chemical recycling, has shown to be promising to break plastics down to fuels, monomers, or other chemicals. This has been shown to also make use of mixed plastic. This work studies the interactions during fast pyrolysis between commonly unrecyclable plastics. Chapter II investigates the interaction of PS and PP in fast pyrolysis at temperatures of 450, 500, and 550 °C with mass ratios of PS:PP at 1:8, 1:1, and 8:1 via a full factorial experimental design. Chapter III investigates the interactions of PS and LDPE at the same temperatures and mass ratios. Using relative areas of extracted ions for pyrolytic products, previous findings were confirmed that the addition of polystyrene to polypropylene and polyethylene increases the amount of light gases produced. Unreported interactions of polystyrene and polypropylene affecting the yield of mid-range hydrocarbon products and styrene were observed, likely due to increased composition range compared to previous studies, providing insight to secondary reactions occurring during co-pyrolysis.

1 Chapter I: Introduction

1.1 Motivation and Background

Yearly global plastic production has increased steadily since 1950, reaching 381 million metric tons in 2015 [1]. In the United States, the Environmental Protection Agency reports approximately 2.7 million metric tons of plastic were reclaimed for recycling out of the 32 million metric tons of plastic produced in 2018 [2]. Of these reclaimed plastics, approximately 600,000 metric tons were non-bottle rigid plastic; composed of 40% high-density polyethylene (#2, HDPE), 36% polypropylene (#5, PP), 13% polyethylene terephthalate (#1, PET), 3% polystyrene (#6, PS), 2% polyvinyl chloride (#3, PVC), <1% low-density polyethylene (#4, LDPE), and 6% unidentified/other plastic resins (#7) [3]. Low-density polyethylene makes up 96% of plastic bag and film in the United States, approximately 430,000 metric tons were reclaimed in 2018 [4]. The overall composition of reclaimed plastic in the United States is shown in **Figure 1-1**.

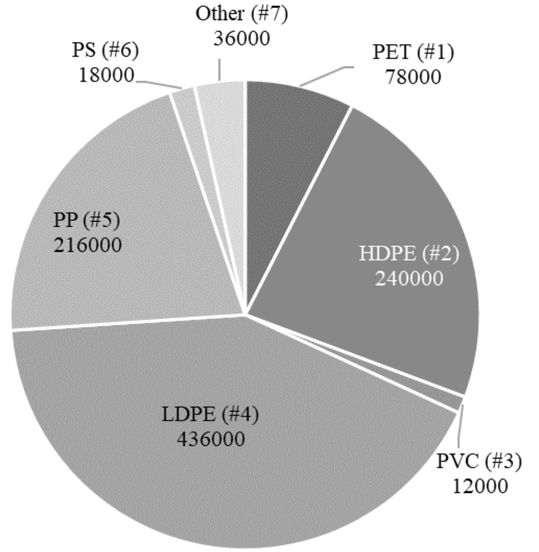


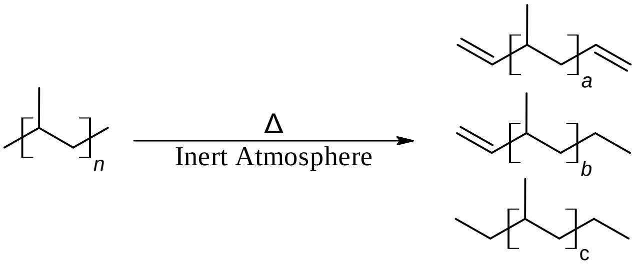
Figure 1-1. Breakdown of reclaimed plastic in the United States including rigid non-bottle plastic and plastic films, data from MORE Recycling [3,4].

Robust recycling collection programs have been developed; however, there is a limitation in the domestic facilities capable of recycling the plastic collected. Prior to 2018, most of the United States' collected recycling was sent to China for recycling or incineration. In 2018, China imposed the National Sword Policy to no longer import most waste plastics. This has led a majority of the plastic collected in the United States to pile up with nowhere to go – where some companies have resorted to paying as much as $25/ton to get rid of recyclable plastics [5]. With approximately one million metric tons of plastic reclaimed, many studies investigating recycling methods to make use of hard-to-recycle polystyrene[6,7], polypropylene[8,9], and low-density polyethylene[9] have been conducted. Even with improvements of traditional recycling, these three plastic types are still only recycled very limitedly, with the highest estimates at 40%, with less than 10% recycled in smaller municipalities [3,4].

Chemical recycling of plastic waste using pyrolysis has demonstrated its ability to produce fuels and commodity chemicals from otherwise unrecyclable plastic waste [10–14]. Pyrolysis is the thermochemical degradation of a polymer in a non-oxidative environment, resulting in production of oligomers and monomers of the original polymer. Another benefit of pyrolysis is the ability to make use of mixed plastic waste without segregation, whereas traditional mechanical recycling requires the sorting of plastic into monostreams [15].

By producing fuels and commodity chemicals, pyrolysis provides an end-of-life for plastic waste, without requiring repeated recycling of the plastics, which ultimately ends with degradation of products requiring the plastic to end up as unrecyclable waste [16,17]. Breaking down the polymer back into smaller, useful chemicals allows the plastic to have a final use. A portion of products can also be used to create new plastics, while most can end up as fuel or commodity chemicals that would otherwise be produced from virgin petroleum.

Each plastic type pyrolyzes to produce different products based on the structure of the original polymer. Polypropylene decomposes to methylated alkene, alkane, and alkadiene products of various chain lengths less than the original polymer chain length, shown in **Figure 1-2**. The breakdown of polyethylene, both high-density and low-density, is shown in **Figure 1-3**, where polyethylene, similar to polypropylene, breaks down to alkane, alkene, and alkadiene products. Polystyrene mostly breaks down into oligomers of styrene along with styrene itself, shown in **Figure 1-4**. These reactions have been proposed to occur via a number of radical mechanisms, including disproportionation, β-scission, hydrogen transfer, and radical recombination[18–21].



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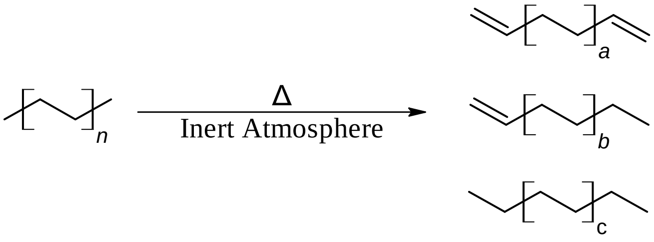

Figure 1-3. Simplified reaction of low-density polyethylene pyrolysis.

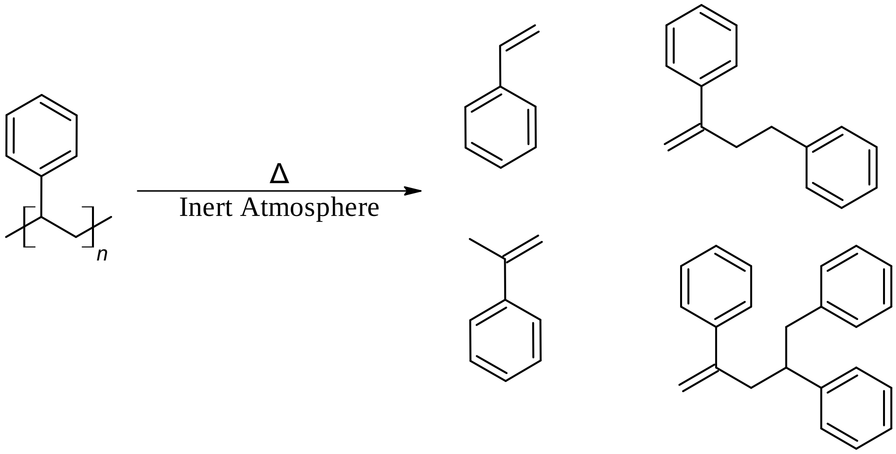

Figure 1-4. Simplified reaction of polystyrene pyrolysis, with products of styrene, methyl-styrene, styrene dimer, and styrene trimer shown.

Studies have found that pyrolysis products, or pyrolyzates, of plastic waste are suitable to be used in fuel [22,23]. Miandad et al found the liquid oil has a high heating value of 41.7-44.2 MJ/kg, which is similar to diesel [14]. This provides the promise of a plastic-based refinery producing commodity chemicals and fuels. A benefit to the inclusion of mixed plastics for pyrolysis is the introduction of aromatic species from the polystyrene, improving the octane factor of the fuel product.

In order to make use of pyrolysis on a large scale, the understanding of interactions occurring in mixed plastic waste must be understood. Application of pyrolysis to mixtures is valuable due to high labor costs of sorting plastic waste along with limitations in automation of plastic sorting [15,24,25]. Pyrolysis has the potential to make use of mixed plastic waste; however, the product distribution found in a variety of mixtures has not been studied. A major limitation in the current work on plastic pyrolysis is the lack of variation in temperature and feedstock composition studied, with many studies focusing on single plastic types [26] or a only on 1:1 mixtures of two plastic types at a single temperature [27].

This work serves to expand the composition and temperature ranges studied to provide insight towards interactions occurring between plastic species and the resulting change in product distribution. Development of these understandings will provide insight towards the products produced from mixtures that are more readily available in industry as refuse from recycling facilities.

1.2 Objectives

The objective of this work is to assess the effects of temperature and feedstock composition on the pyrolysis products of mixed plastic waste, particularly polypropylene, polystyrene, and low-density polyethylene at temperatures of 450, 500, and 550°C with mass ratios of 1:8, 1:1, and 8:1. By investigation of composition and temperature in blended plastic mixtures, pyrolytic temperature adjustments can provide background for the tuning of desired products, such as fuel-range hydrocarbons to be later refined into market-grade products. This work also provides the background to identify components to be analyzed in the development of a kinetic model of the mixed plastic waste.

1.3 Thesis Organization

In this thesis, two research papers investigating the effects of temperature and mass ratios on plastic mixtures composed of polystyrene-polypropylene and polystyrene-low-density-polyethylene. The first paper has been submitted for peer review according to the below citation. The second paper was, or will be, submitted for peer review according to the second citation.

(1) Meduna, Z., Kubatova, A., Klemetsrud, B., Experimental Investigation of Co-Pyrolysis of Waste Polystyrene and Polypropylene Product Distribution with Temperature and Compositional Changes. *J. Anal. Appl. Pyrolysis.*

(2) Meduna, Z., Kubatova, A., Klemetsrud, B., "Experimental Investigation of Co-Pyrolysis of Waste Polystyrene and Low-Density Polyethylene at Varying Temperature and Feedstock Composition." *ACS Sustainable Chem. & Eng.*

This thesis is comprised of four chapters, described below:

Chapter I introduces the principles of chemical recycling and pyrolysis as motivations to this work, along with objectives of this work.

Chapter II is the first research paper mentioned above, describing a background to polystyrene-polypropylene investigations, experimental methods, and results of the study.

Chapter III is the second research paper mentioned above, with background on polystyrene-polyethylene investigations, experimental methods, and results of the study.

Chapter IV summarizes the project findings including recommendations for future work.

2 Chapter II: Experimental Investigation of Co-pyrolysis of Waste Polystyrene and Polypropylene Product Distribution with Temperature and Compositional Changes

Submitted to JOURNAL OF ANALYTICAL AND APPLIED PYROLYSIS
MEDUNA, Z, KUBATOVA, A, KLEMETSRUD, B. EXPERIMENTAL INVESTIGATION OF CO-PYROLYSIS OF WASTE POLYSTYRENE AND POLYPROPYLENE PRODUCT DISTRIBUTION WITH TEMPERATURE AND COMPOSITIONAL CHANGES

Abstract

Plastics are widely used in a variety of applications; however, there are limited processes in place for recycling at the end of their life. Pyrolysis, or chemical recycling, has shown to be promising to break plastics down to fuels, monomers, or other chemicals. A major constraint of traditional, mechanical recycling is the requirement of sorting between plastic types; however, pyrolysis has the potential to make use of mixed plastic waste. To take advantage of mixed plastic waste, an understanding for interactions between plastic species must be developed. This study investigates the interaction of polystyrene and polypropylene in fast pyrolysis at temperatures of 450, 500, and 550 °C with mass ratios of polystyrene-polypropylene at 1:8, 1:1, and 8:1 via a full factorial experimental design. 80-150 μg samples were pyrolyzed using a micro-pyrolyzer hyphenated to GC-MS. Using relative areas of extracted ions for pyrolytic products, previous findings were confirmed that the addition of polystyrene to polypropylene increases the amount of light gases produced. Unreported interactions of polystyrene and polypropylene affecting the yield of mid-range hydrocarbon products and styrene were observed, likely due to increased composition range compared to previous studies, providing insight to secondary reactions occurring during co-pyrolysis.

2.1 Introduction

Plastic is a staple of daily life, ranging from food packaging to automobile components. Plastic is seen as an inexpensive, reliable material for a wide range of applications; however, plastic is often found in single-use applications, creating substantial amounts of waste. Single use plastic production has increased over the years, with approximately 32%, or 25 million tons, entering the environment every year [17,28]. Even if properly disposed of, these waste products often go unrecycled due to limitations in mechanical recycling. Plastics that are accepted into mechanical recycling facilities undergo degradation of the polymer, resulting in down-cycling of plastic waste to a lower quality product. Overall, 95% of plastic packaging value exits the “closed loop” after its first use [17]. For example, traditional mechanical recycling of polypropylene and low-density polyethylene cause the materials to thermo-mechanically degrade significantly, resulting in approximately 25% reduction in tensile strength after five rounds of recycling [3]. Due to this degradation, polypropylene is often downcycled after a single use to textiles or playground equipment [29].

Plastic types 3-7 go mostly unrecycled, often passing through recycling facilities to be landfilled or incinerated [30]. These include polyvinyl chloride (PVC, #3), low density polyethylene (LDPE, #4), polypropylene (PP, #5), polystyrene (PS, #6), and other types of plastics (#7). In 2018, 36% of non-bottle rigid plastic waste was polypropylene and 3% was polystyrene, making up nearly 500 million pounds of unrecyclable waste in the United States [3].

Pyrolysis, or chemical recycling, provides the opportunity to use plastics that are not traditionally recycled – producing fuels, monomers, and/or other chemicals [12]. A major constraint to traditional recycling is the need for sorting of plastic waste due to the wide variety of plastics in use, along with contamination of food and residues on or within the plastic [30]. While there is improvement in the sorting of plastics into monostreams, approximately one-third of plastic waste cannot be sorted using advanced automation [15]. Developing an understanding of mixed plastic pyrolysis without sorting provides framework to create a plastic-based refinery to reduce the demand for virgin petrochemical products and provide a solution to the plastic waste environmental problem.

Many researchers have studied individual plastic types [18,19,31,32] and mixtures [20,33,34] with a primary focus using thermogravimetric analysis (TGA). These studies have been limited to slow pyrolysis [34–36]; for example, Ciliz et. al. heated at a rate of 5 °C/min with a hold time of 15 minutes after the final temperature was achieved [35]. With such long residence times, large scale applications may become impractical – leading to the investigation of fast pyrolysis with analysis of products produced, opposed to the limited mass loss data found in TGA. Other studies that focus on product distributions are limited in mixture compositions and temperatures studied. Williams and Williams found that with slow pyrolysis at heating rates of 25 °C min^{-1} to 700°C with 1:1 plastic mixtures interactions did occur; however, these interactions have not been reported in more practical applications of fast pyrolysis [13].

On-line pyrolysis GC-MS (Py-GC-MS) allows for identification and quantitation of what would be considered liquid oil and non-condensable gases collected from standalone pyrolysis systems. Previous work with Py-GC-MS focuses on fast pyrolysis at a single temperature to investigate primary reactions of pyrolysis [26]. More recent work on mixed plastic studied interactions between plastic types at a single temperature with only one level of plastic compositions [27].

This study combines factors of plastic feedstock compositional changes and temperature to assess the significant effects on the pyrolytic products. Using a factorial design of experiments, the factors of temperature and composition can be analyzed along with their interactions with statistical reinforcement. This work also includes analysis of light gases formed in fast pyrolysis, allowing for assessment of interactions otherwise unstudied in recent work [27]. This understanding of significant effects will allow for further analysis and optimization for the pyrolysis of plastic waste to fuels or other useful chemicals.

This work also uses the benefits of evolved gas analysis mass spectrometry (EGA-MS) for preliminary temperature screening. By replacing the separative column with a deactivated capillary, a Py-GC-MS system can be used to evaluate the evolved gases with a temperature gradient in the pyrolysis furnace. This gives a total ion current (TIC) providing information similar to that of derivative thermogravimetry (DTG) [10,36], where the mass loss found in DTG would be proportional to ion response in EGA-MS. EGA-MS proves to be advantageous compared to DTG and TGA by providing mass spectral data to gain insight towards the size, and in some cases, type, of molecules produced at a given temperature at faster heating rates than traditionally used in TGA analysis. These EGA-MS experiments also provide insight for temperatures ideal for fast pyrolysis for single-shot Py-GC-MS experiments. It is important to focus on pyrolytic temperatures where both plastic types are producing gaseous products, as gas-phase radical species [18,19,36] could cause interactions to produce new products or affect reaction rates.

2.2 Experimental Methods

2.2.1 Instrument Parameters

All pyrolysis GC-MS (Py-GC-MS) experiments were conducted using a Frontier 3030-D Multi-Shot Pyrolyzer, equipped with the Auto-Shot Sampler AS-1020E, and Microjet Cryotrap MJT-1035E. This on-line pyrolyzer was used in conjunction with an Agilent 7890A Gas Chromatograph with an Agilent 5975C Mass Spectrometer. The stationary phase used was a Frontier Ultra ALLOY+5 capillary column (30 m x 0.25 mm x 0.25 μm) with a helium mobile phase (1.0 mL min^{-1}) with an injector split ratio of 1:50.

All evolved gas analysis (EGA) GC-MS experiments were conducted using the same online pyrolyzer and gas chromatograph; however, a Frontier deactivated EGA tube (2.5 m x 0.15 mm) was used in place of the separation column.

For EGA and GC modes, the MS data in total ion chromatograms (TIC) were acquired in the mass range of 35-750 *m/z* and 10-600 *m/z* at a scan rate of 6.00 and 2.66 scan/s, respectively. The electron ionization was employed with setup at 70 eV. No MS solvent delay was needed.

2.2.2 Gas Chromatograph and Pyrolysis Furnace

For Py-GC-MS experiments, the GC oven was programmed for 40°C for 1 minute, 25°C/minute to 320°C, held at 320°C for 16 minutes. The pyrolysis furnace was programmed for single-shot pyrolysis at the set temperature for 0.5 minutes to ensure complete pyrolysis.

For EGA-MS experiments, the GC oven was held at 300°C for the entirety of the pyrolyzer temperature ramp for a total time of 9.6 minutes. The pyrolysis furnace was held at 300°C for 0.8 minutes, then increased to 700°C at a ramp rate of 50°C/min, with a final hold time of 0.8 minutes.

2.2.3 Sample Material and Preparation

Plastic samples were procured from the on-campus dining center and ground using liquid nitrogen in a flour grinder. These samples were sieved to contain only particles smaller than 250 microns. Polypropylene used was a Pactiv EarthChoice container, noted as a mineral filled polypropylene (MFPP). Polystyrene used was a PXT-900 container, defined as oriented polystyrene (OPS). Plastic types were weighed and combined to the appropriate mass ratios for analysis.

All samples were introduced to the pyrolyzer via autosampler in 80 μL deactivated stainless steel cups with typical weights of 30-150 μg measured by microbalance.

2.2.4 Experimental Design

A general full factorial design with two factors, temperature and polystyrene fraction, was used. Temperature had three levels: 450°C, 500°C, and 550°C. Polystyrene mass fraction had three levels: 11.1 wt%, 47.8 wt%, and 88.3 wt% (labeled 8:1, 1:1, 1:8 PP:PS, respectively).

Table 2-1 contains the experimental matrix used. These three levels were chosen to screen a wide range of composition while maintaining adequate mass spectral response for data analysis, determined by evolved gas analysis (EGA). The design was conducted with three replicates at all points allowing for elimination of outliers, if necessary. All trials of the same composition were run on the same day in sequence of low to high temperature.

This was done to limit contamination between samples and reduce the need for cooling air and time required between samples.

Table 2-1. Two Factor, Three Level Full Factorial Experimental Design

Replicates		Temperature		
		450°C	500°C	550°C
PP:PS Mass Ratio	8:1	3	3	3
	1:1	3	3	3
	1:8	3	3	3

2.2.5 Data Processing

Sample chromatograms and mass spectral data were analyzed using Agilent MSD Chemstation (version F.01.03.2365). Peak area percentages were analyzed using target ion 43 *m/z* for polypropylene related products. Ion 104 *m/z* was used for styrene, while ion 91 *m/z* was used for other polystyrene related products. These ions are consistent with those used by Coralli et al for quantitation [27]. This allows for comparative analysis between samples of different mass, using the relative peak area as a percentage of the overall area from the products related to the respective polymer. All compounds were integrated by their base peak of the selected ion described previously, then calculated to a relative peak area given by the product peak area over the sum of the product areas from the appropriate polymer.

All compounds were identified based on the NIST05 database and/or comparing to mass spectral data and retention found in Pyrolysis-GC-MS Data Book of Synthetic Polymers [37].

2.3 Results and Discussion

2.3.1 Single Species Evolved Gas Analysis

Figure 2-1 displays the thermogram results of polystyrene and polypropylene. The major production of products for polystyrene is in the range of 400-500°C, which matches DTG results in literature at a heating rate of 100°C/min [38]. The rate of mass loss from DTG results is analogous to the abundance reported from the mass spectrometer. Degradation of polypropylene is found in most abundance between 450 and 550°C, which is also reinforced from DTG results using a temperature heating rate of 10°C/min [36]. While the same mass of samples were analyzed, the total ion current (TIC) abundance for polypropylene was much lower than polystyrene. This is likely due to variation in the yield of ions produced from electron impact ionization (EI) [39].

These comparative results justify the use of waste plastic for this research, as it is shown their degradation temperatures are comparable to studies using standard reference materials [10,36,38].

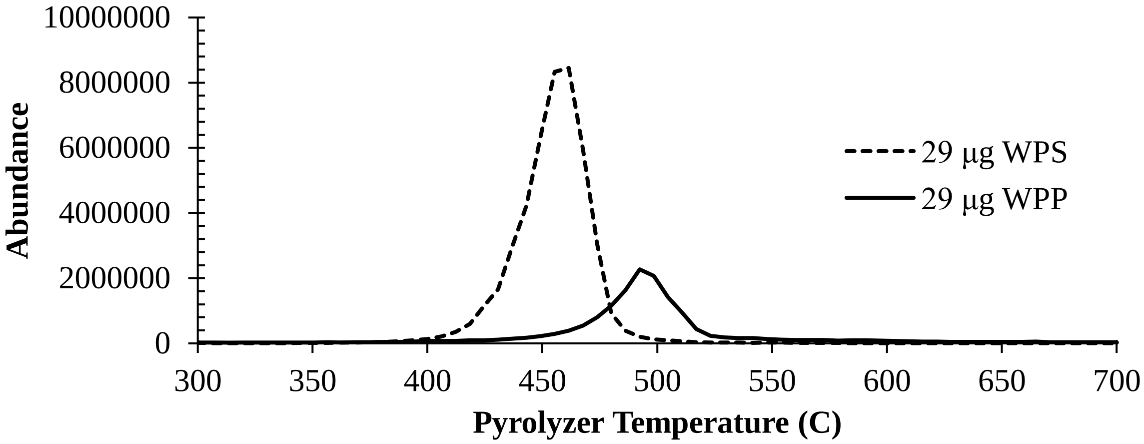

Figure 2-1. Thermograms from evolved gas analysis (EGA-MS) of waste polystyrene (WPS) and waste polypropylene (WPP) in the temperature range of 300 to 700 °C at a temperature ramp rate of 50°C/min.

2.3.2 Binary Mixture Evolved Gas Analysis

The thermograms for binary mixtures of polystyrene and polypropylene are shown in **Figure 2-2a**. In the 1:1 and 8:1 PP:PS mixtures, the two distinct profiles shown in **Figure 2-1** are slightly convoluted, yet still distinct to recognize the pattern from. This indicates the pyrolytic temperatures for both species are somewhat independent in a mixture. For the 1:8 WPP:WPS mixture, the total ion thermogram does not display any significant polypropylene product, likely due to the high ionization rate of aromatics by the mass spectrometer, producing a wider band for the large amount of polystyrene.

Figure 2-2b shows the extracted ion thermogram of 1:8 PP:PS mixture, showing the distinction between the production of styrene (ion 104 *m/z*) and branched alkenes (ion 69 *m/z*) from polystyrene and polypropylene, respectively. This indicates that the mixture does indeed have products of pyrolysis from polypropylene in low abundance. This very low response is also indicative of the lower ionization of alkenes and alkanes compared to aromatics, not necessarily a lower pyrolytic rate – similar to what is shown in **Figure** where the results for the same mass of plastic are nearly a third the response of polystyrene for polypropylene.

Figure 2-2c shows the extracted ion thermogram of 1:1 PP:PS mixture, showing the distinction between the production of styrene (ion 104 *m/z*) and branched alkenes (ion 69 *m/z*) from polystyrene and polypropylene, respectively. From the overlap of the extracted ion thermograms for polystyrene and polypropylene when pyrolyzed as a mixture, the temperatures of interest were determined to be at temperatures >450°C for both polymers to produce gaseous products for potential interactions.

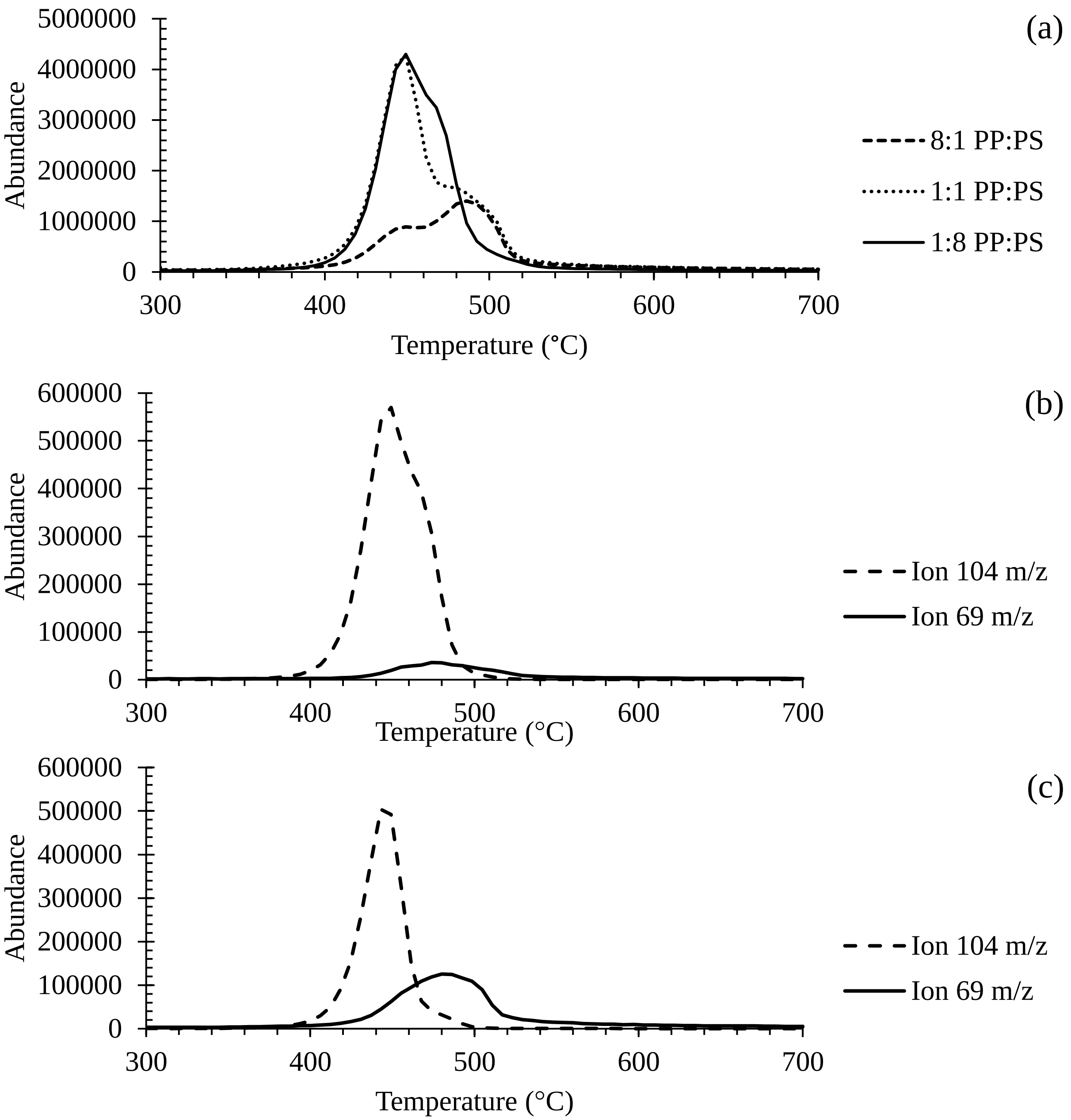

Figure 2-2. (a) Thermograms from evolved gas analysis for binary mixtures of PS and PP in the temperature range of 300 to 700 °C at a ramp of 50°C/min. **(b)** Extracted ion thermograms from evolved gas analysis for 1:8 PP:PS mixture at the same temperature program. **(c)** Extracted ion thermograms from evolved gas analysis for 1:1 mixture of PS and PP at the same temperature program. Ion 104 *m/z* indicates styrene, produced from

polystyrene. Ion 69 *m/z* indicates the prevalent ion produced from branched alkanes and alkenes products of polypropylene.

2.3.3 Individual Plastic Species Pyrolysis-GC-MS

Figure 2-3 contains the total ion current (TIC) of pyrolysis products from waste polypropylene. The spread of alkadiene, alkene, and alkane products ranging in molecular weight is consistent with literature; with the selected products of interest: propene (C3), n-pentane (C5), 2,4-dimethyl-heptene (C9), trimethyl-nonene (C12), tetramethyl-undecene (C15), pentamethyl-tridecene (C18), and hexamethyl-pentadecene (C22); consistent with identification by [36,37,40].

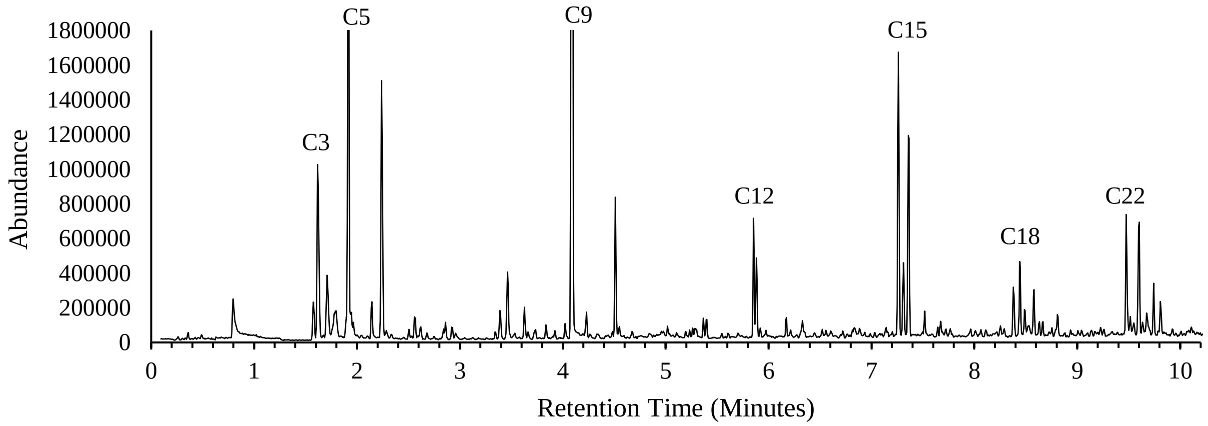

Figure 2-3. Total ion current of pyrolysis products of waste polypropylene at 450°C for 30 seconds.

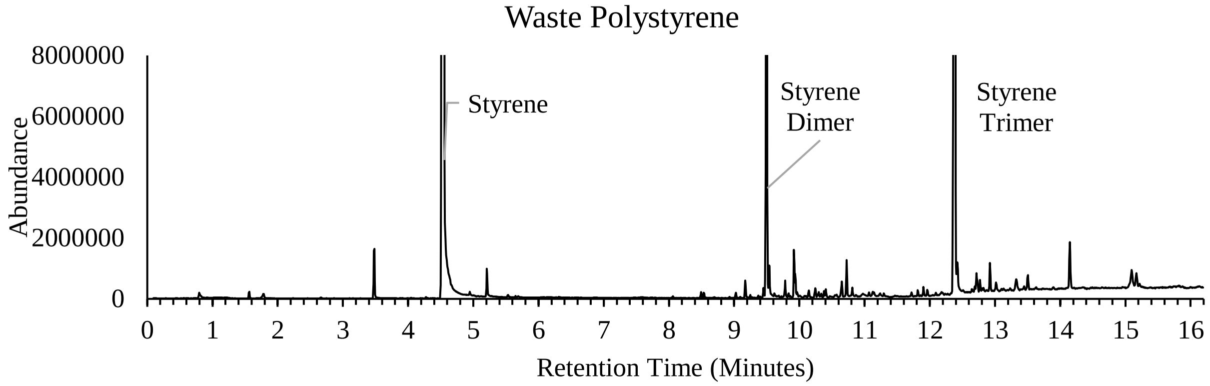

Figure 2-4. Total ion current (TIC) of pyrolysis products of waste polystyrene at 450°C for 30 seconds.

Figure 2-4 shows the three major products identified from polystyrene: styrene, styrene dimer, and styrene trimer. Consistent with previous work [11,37], these compounds were selected for analysis based on high abundance for integration and comparisons.

2.3.4 Binary Mixture Pyrolysis-GC-MS Analysis

Figure 2-5 shows the major products from polypropylene and polystyrene pyrolysis labeled on the total ion current of 1:1 polystyrene-polypropylene. With the convolution of peaks, particularly with C22 and the styrene dimer, the need for analysis of extracted ions, as opposed to the TIC signal, is evident to prevent misinterpretation of data.

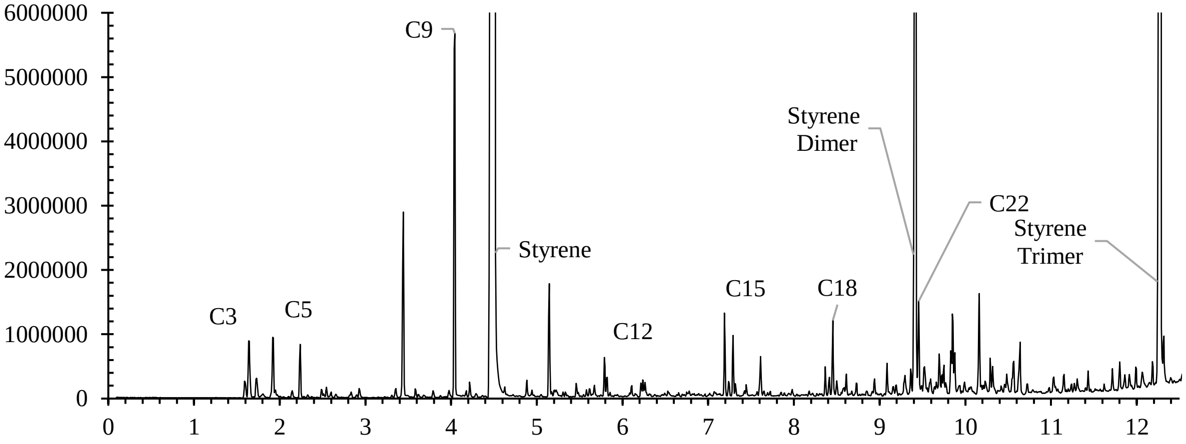

Figure 2-5. Total ion current (TIC) of pyrolysis of 1:1 polypropylene-polystyrene at 500°C for 30 seconds.

The variation in relative peak areas for polypropylene and polystyrene products due to compositional changes at 450, 500, and 550°C are shown in **Figure 2-6**. All components show some variation between the three compositional levels in the design; however, from the factorial regression, most of these variations are not statistically significant, as shown in **Table 2-2** ($p > 0.05$). Notably, at 500 °C and 550 °C, there is an increase in the production of C3 hydrocarbons from polypropylene as the polystyrene fraction increases ($p < 0.05$), similar to that seen by Williams and Williams [13] in contradiction to the absence of interactions reported by Coralli et al. [27]. With this being most significant at higher temperatures, the interaction between temperature and composition would be anticipated as significant; however, it is not (p=0.14). This increase in C3 hydrocarbon production is likely due to secondary reactions between the plastic species, potentially a catalytic effect of cracking heavier hydrocarbons by aromatic species produced from polystyrene. For polystyrene products, there is an increase in the relative amount of styrene and a decrease in the styrene dimer and trimer as the proportion of polypropylene increases. These previously unreported trends imply that the introduction of polypropylene increases the production of styrene or the conversion of the oligomers towards unanalyzed products via secondary reactions such as adduct formation.

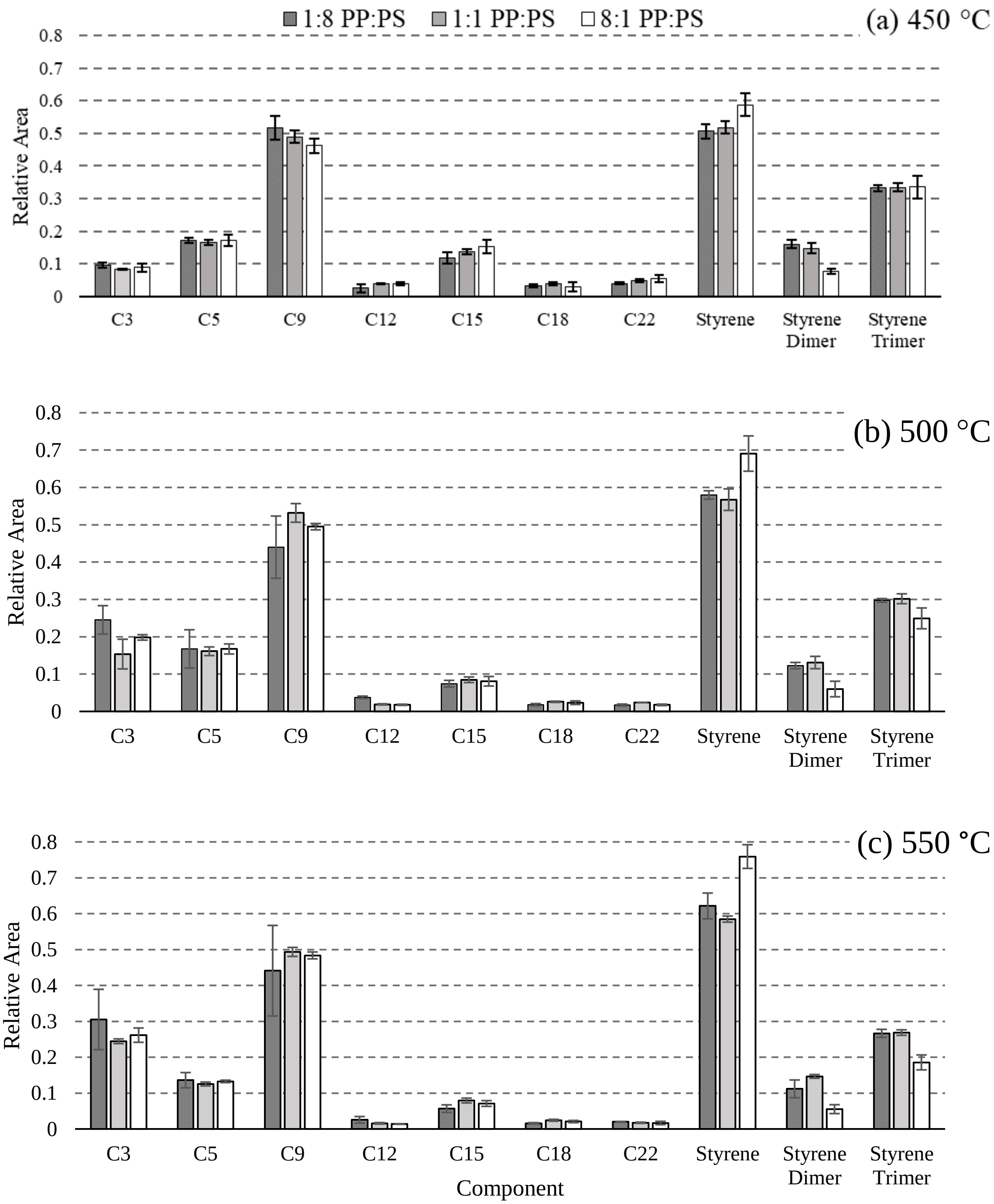

Figure 2-6. Relative extracted ion peak areas produced from pyrolysis of polystyrene-polypropylene mixtures with varying feedstock composition at (a) 450°C (b) 500°C (c) 550.

The change in relative area for both polystyrene and polypropylene products due to temperature ranging from 450 to 550 °C with the three levels of composition is shown in **Figure 2-7**. For polypropylene related compounds: an increase in temperature shows an increase of C3 with a decrease in the larger hydrocarbons analyzed (C5+). Polystyrene-based compounds show the same trend, with an increase in styrene with temperature while the oligomers decrease with temperature. All components were significantly affected by temperature, as shown in **Table 2-2** ($p < 0.05$).

In **Figure 2-7b** and **7c**, a lack of change in relative abundance of C9 with respect to temperature is shown. There appears to be a maximum within the range of 450 to 550°C, as relative areas at 450 and 550°C are nearly the same with an increased relative area at 500°C. This maximum production of C9 hydrocarbon occurs between 450 and 550°C, which could be optimal for fuel range products.

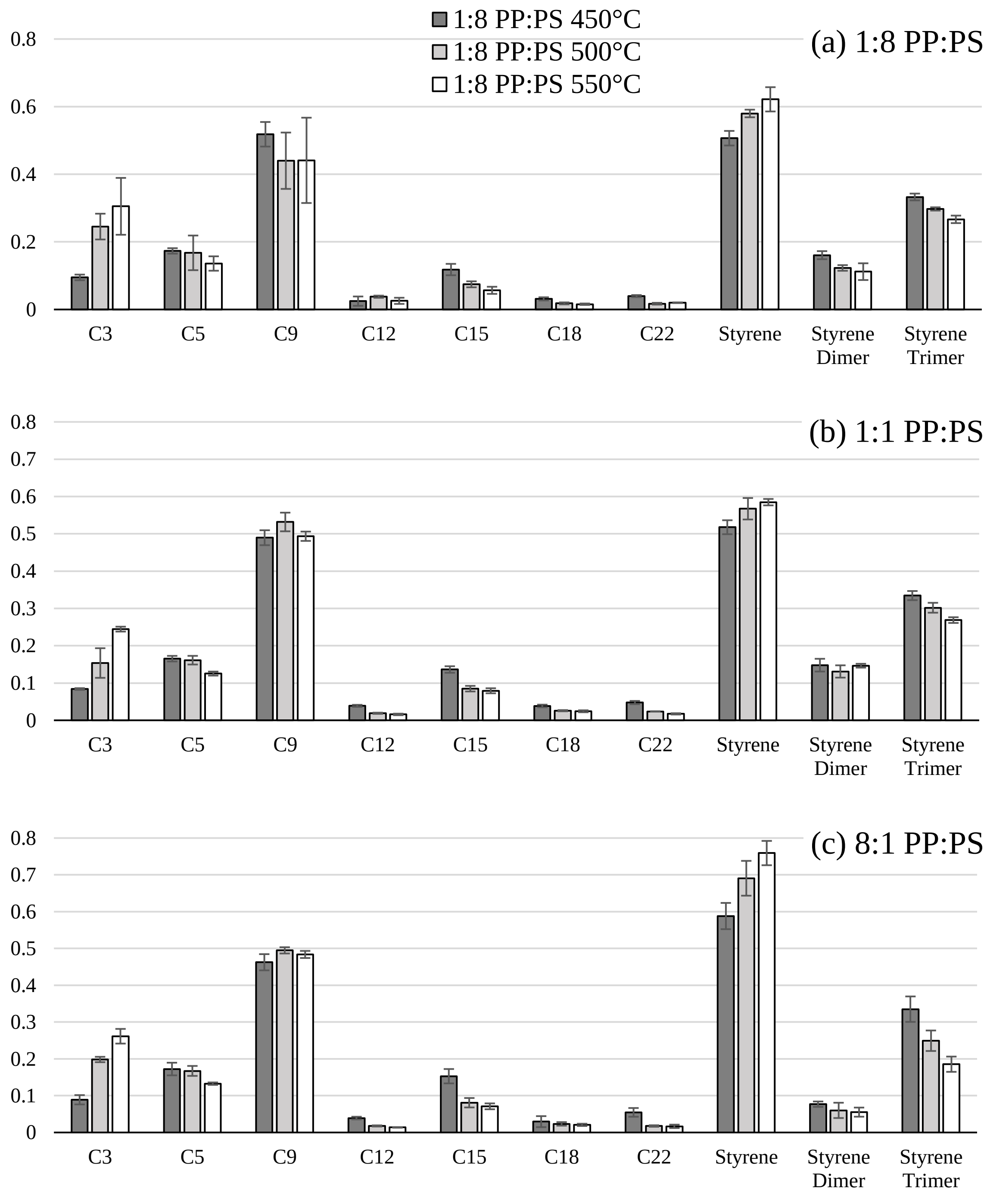

Figure 2-7. Relative extracted ion peak areas for selected compounds produced from pyrolysis of polystyrene and polypropylene with varying pyrolysis temperatures of 450, 500, 550°C and varying mass proportions of polypropylene-polystyrene at (a) 1:8, (b) 1:1, and (c) 8:1.

To make use of the large dataset, a factorial regression was performed using Minitab. **Table 2-2** contains the p-values from the factorial design for the factors of temperature and composition on the relative areas of the listed compounds. All statistically significant p-values are *italicized*. As discussed above: all components were significantly affected by changes in temperature ($p<0.05$); however, not all components had a statistically significant difference due to change in composition. Only compounds produced by polystyrene along with C3 and C15 from polypropylene were significantly affected due to composition of the plastic mixture ($p<0.05$). The increase in light hydrocarbons with addition of polystyrene to polypropylene along with an increase in styrene in polystyrene-propylene mixtures would provide tunability in the proportion of gaseous fuels and C15 fuel components produced from polypropylene and the amount of styrene monomer produced to be used to manufacture new polystyrene.

Table 2-2. Factorial Regression Results for Analyzed Compounds

Compound	Composition P-Value	Temperature P-Value	Temperature × Composition P-Value
C3	0.001	<0.001	0.139
C5	0.759	<0.001	0.994
C9	0.230	<0.001	0.205
C12	0.202	0.006	0.003
C15	0.023	0.000	0.191
C18	0.055	0.010	0.447
C22	0.213	<0.001	0.214
Styrene	<0.001	<0.001	0.041
Styrene Dimer	<0.001	0.001	0.133
Styrene Trimer	<0.001	<0.001	0.002

2.4 Conclusions

In this work, the fast pyrolysis of waste polystyrene and polypropylene were analyzed using Pyrolysis/GC-MS at temperatures of 450, 500, and 550°C for 30 seconds. It was determined that there was significant impact of temperature on product composition for the binary mixtures of polypropylene and polystyrene, as expected [18–20,36,40]. Feedstock composition only had a significant impact on product composition for C3, C15, styrene, styrene dimer, and styrene trimer. The impact of polystyrene increasing production of light gases, such as C3, was expected as previously reported [13]. Interactions due to secondary reactions of polystyrene and polypropylene seen to impact the relative abundance of C15, styrene, styrene dimer, and styrene trimer are not observed in other studies involving this binary mixture, likely due to limited composition ranges observed in previous work by Coralli et al. 2022 and Williams and Williams 1999 [13,27].

This work provides background for investigation of interactions between plastic types in the form of secondary reactions for the use of Py-GC-MS for analysis of mixed plastic samples and applications towards chemical recycling of plastic waste.

CRediT Authorship Contribution Statement

Z. Meduna: Formal analysis, Methodology, Investigation, Validation, Writing – Original Draft. **B. Klemetsrud:** Supervision, Funding acquisition, Conceptualization, Writing – Review & Editing. **Alena Kubátová:** Supervision, Methodology, Validation

Acknowledgements

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3 Chapter III: Experimental Investigation of Co-Pyrolysis of Waste Polystyrene and Low-Density Polyethylene at Varying Temperature and Feedstock Composition

Abstract

Low-density polyethylene and polystyrene are two of the most common plastics found in packing materials, with millions of tons produced and disposed of each year. In this study, the fast pyrolysis of waste polystyrene and low-density polyethylene were studied using pyrolysis-GC-MS at temperatures of 450, 500, and 550 °C for 30 seconds at mass ratios of 1:8, 1:1, and 8:1. It was determined there was a significant impact by temperature on the product composition for all mixtures of polyethylene and polystyrene, increasing production of light hydrocarbons. This study also found previously unreported interactions between polyethylene and polystyrene upon pyrolysis at 450-550°C in mass ratios of 8:1, 1:1, and 1:8. These interactions resulted in 50% increase light hydrocarbon response with increased polystyrene fraction at all temperatures along with variations up to 30% in mid-range and heavy hydrocarbons produced by polyethylene with variation in polystyrene fraction.

3.1 Introduction

Across the world, plastic products are used as grocery bags, packaging, and food containers; however, many of these plastics are not ultimately recycled, even when properly disposed of by the consumer. In 2018, at least 96 percent of the 453,000 metric tons of plastic film reclaimed in the United States were low-density polyethylene (LDPE), while only 47 percent was recycled [4]. Some of this reclaimed, unrecycled plastic is incinerated for energy recovery while the rest is landfilled. LDPE is the most common plastic used as mulch in agriculture [41], leading to a large amount of LDPE dispersed into the environment. Low-density polyethylene also enters the environment due to unmanaged dumping or litter [15]. Along with polystyrene (PS), the low density of LDPE often causes the waste to be carried by wind from uncovered landfills. Due to this, polyethylene and polystyrene are two of the most abundant types of plastics in coastal waters of the Mediterranean [42].

Pyrolysis, or thermal decomposition under an oxygen-free environment, shows potential to make use of unrecycled plastic waste, producing fuels and commodity chemicals. Pyrolysis is mostly suggested for polymers that cannot be easily depolymerized or mechanically recycled, particularly polymers such as polystyrene, polypropylene, and low-density polyethylene [15]. Polyethylene's high molecular weight (e.g., 30,000 – 500,000 Da) with minimal branching, even in low-density forms, pyrolyzes to produce a homologic series of alkanes, alkenes, and dienes ranging in chain of four to five carbons in length up to lengths larger than forty carbons. These products have made the pyrolysis of polyethylene a potential pathway to produce chemical intermediates or fuel additives [43,44]. Sharma et al found that waste polyethylene produces alternative diesel fuel, which is suitable to be used on its own or in a blend with petroleum diesel fuel [23]. Polystyrene, commonly seen as Styrofoam, pyrolyzes to produce toluene, styrene, along with short oligomers of styrene such as a dimer and trimer [27]. In a combination polystyrene and low-density polyethylene, commonly found together in packaging waste, co-pyrolysis may provide fuel-grade products with aromatic content similar to gasoline.

Many studies have only focused on the pyrolysis of polyethylene and polystyrene in their pure form, without consideration for mixtures of plastic types [23,32,43,45,46]. These investigations are not feasible in large-scale plastic pyrolysis facilities where heavy comingling and contamination of plastic feedstocks are seen [30] . Pyrolysis is proposed to occur through reactive intermediates for polyethylene, polystyrene, and polypropylene [18,19,21]. The reactive intermediates could potentially result in interactions between plastic species by inhibiting pyrolysis, promoting pyrolysis, or resulting in adduct formation. Many studies have included the analysis of individual plastic types [18,19,31,32] and a variety of mixtures [20,33,34], primarily focused on slow pyrolysis via thermogravimetric analysis [34–36]. However, current studies do not investigate product distribution of fast pyrolysis at a variety of temperatures and feedstock composition, limiting the understanding of how plastics would behave in a variety of conditions.

This study made use of evolved gas analysis mass spectrometry (EGA-MS) to screen potential pyrolytic temperatures. EGA-MS experiments were conducted using the same on-line pyrolysis GC-MS system; however, the capillary column was replaced with a short deactivated alloy capillary tube held under a constant oven temperature. This provides total ion current response from the mass spectrometer directly from the inlet pyrolyzer without separation of pyrolyzates. Based on the pyrolysis furnace temperature at a given time, results provided are analogous to what is found by thermogravimetric analysis [38,47]. However, the benefit to EGA-MS is ability to provide insight on the size and type of pyrolysis products at a given temperature. This gives insight towards temperatures ideal for fast pyrolysis experiments. In mixtures, it is important that both plastic species are pyrolyzing at the set furnace temperature to ensure their co-pyrolysis. Another consideration is the range of products produced, while high temperatures such as 800°C will ensure pyrolysis, products in the range of fuel (C_8-C_{20}) will be reduced with increased production of light hydrocarbons ($<C_4$). While increased light hydrocarbons will provide gaseous fuels, the major target of this work is to produce liquid fuels capable of replacing those produced from fossil resources. To focus on fuels, this work will target lower temperatures where fuel-range products are more abundant.

In this study, fast pyrolysis of mixed plastic waste was investigated, focusing on distribution patterns of a wide range of hydrocarbon. The hydrocarbon profiles from C4 to C39 were investigated as representative products of LDPE pyrolysis and compared to characteristic PS products: toluene, styrene, styrene dimer, and styrene trimer. Temperature and feedstock composition were investigated for production of the wide range of hydrocarbons produced. To provide statistical reinforcement of findings, in this work, a two factor, three level, full factorial design is used to validate significant effects on the relative amount of each pyrolysis product by temperature and feedstock composition. The understanding of significant effects will lay the groundwork for further analysis and optimization to produce fuels and commodity chemicals from mixed plastic waste.

3.2 Experimental Methods

3.2.1 Instrument Parameters

All pyrolysis GC-MS (Py-GC-MS) experiments were conducted using a Frontier 3030-D Multi-Shot Pyrolyzer, equipped with the Auto-Shot Sampler AS-1020E, and Microjet Cryotrap MJT-1035E. This on-line pyrolyzer was used in conjunction with an Agilent 7890A gas chromatograph (GC) with an Agilent 5975C mass spectrometer (MS). The capillary column used was a Frontier Ultra ALLOY+5 (28 m x 0.25 mm x 0.25 μm) with helium carrier gas (1.0 mL min^{-1}) with a GC injector in split mode with a ratio of 1:50.

All evolved gas analysis (EGA) and GC-MS experiments were conducted using the same online pyrolyzer and gas chromatograph; however, a Frontier deactivated EGA tube (2.5 m x 0.15 mm) was used in place of the separation column for EGA-MS experiments.

For EGA and GC modes, the MS data in total ion chromatograms (TIC) were acquired in the mass range of 35-750 *m/z* and 10-600 *m/z* at a scan rate of 6.00 and 2.66 scan/s, respectively. The electron ionization was employed with setup at 70 eV. No MS solvent delay was needed.

3.2.1.1 Gas Chromatograph and Pyrolysis Furnace

For Py-GC-MS experiments, the GC oven was programmed for 40°C for 1 minute, 25°C/minute to 320°C, held at 320°C for 16 minutes. The pyrolysis furnace was programmed for single-shot pyrolysis at the set temperature for 0.5 minutes to ensure complete pyrolysis.

For EGA-MS experiments, the GC oven was held at 300°C for the entirety of the pyrolyzer temperature ramp for a total time of 9.6 minutes. The pyrolysis furnace was held at 300°C for 0.8 minutes, then increased to 700°C at a ramp rate of 50°C/min, with a final hold time of 0.8 minutes.

3.2.2 Sample Material and Preparation

Polystyrene was procured from the on-campus dining center while low-density polyethylene was from an ice cream pale. The LDPE was AirLite linear low-density polyethylene. Polystyrene used was a PXT-900 container, described as oriented polystyrene (OPS). Plastics were ground using liquid nitrogen in a YaeMarine 150 g grain mill grinder. These samples were sieved to contain only particles smaller than 250 microns then weighed and combined to the appropriate mass ratios for analysis.

All samples were introduced to the pyrolyzer via autosampler in 80 μL deactivated stainless steel cups with typical weights of 30-150 μg measured by microbalance.

3.2.3 Experimental Design

A general full factorial design with two factors, temperature and polystyrene fraction, was used. Temperature had three levels: 450°C, 500°C, and 550°C. Polystyrene mass fraction had three levels: 10.9wt%, 49.5 wt%, and 87.8 wt% (labeled 8:1, 1:1, 1:8 LDPE:PS, respectively).

Table 3-1 contains the experimental matrix used. These three levels were chosen to screen distribution profiles of products at varying conditions while still allowing for response from the components from the less abundant plastic type. The design was conducted with four replicates at all points allowing for elimination of outliers as needed. All trials of the same composition were run on the same day in sequence of low to high temperature. This was done to limit contamination between samples and reduce the need for cooling air and time required between samples.

Experimental data was analyzed using Minitab analysis of variance.

Table 3-1. Two Factor, Three Level Full Factorial Experimental Design

Replicates		Temperature		
		450°C	500°C	550°C
LDPE:PS Mass Ratio	8:1	4	4	4
	1:1	4	4	4
	1:8	4	4	4

3.2.4 Data Processing

The thermograms (EGA-MS) and Py-GC-MS data were processed using Agilent MSD Chemstation (version F.01.03.2365) and Agilent MassHunter MS Quantitative Analysis (build 10.2.733.8). Peak area percentages were analyzed using target ions consistent with the NIST20 database along with being consistent with those used by Coralli et al. for quantitation of polystyrene [27] and Steinmetz et al for polyethylene [48]. All compounds were integrated by their base peak of the selected ion, then calculated to a relative peak area given by the product peak area over the sum of the product areas from the appropriate polymer. Using relative areas respective to products from the same polymer, comparative analysis between samples of different mass was achieved. Details on relative peak area calculations and ions selected can be found in **Appendix B**.

All compounds were identified based on the NIST20 database and/or comparing to mass spectral data and retention profile corresponding to data reported in Pyrolysis-GC-MS Data Book of Synthetic Polymers [37].

3.3 Results and Discussion

3.3.1 Single Plastic EGA-MS

Figure 3-1 shows the thermogram produced by evolved gas analysis (EGA) of polystyrene and low-density polyethylene. The rate of mass loss from DTG or TGA results is analogous to the abundance acquired by the MS, but not directly proportional due to varying ionization response seen in electron ionization (EI) [39] . The major production of products for polystyrene is in the range of 400-500°C, which agrees with DTG results in literature at a heating rate of 100°C/min [38]. Degradation of LDPE is found to begin at approximately 450°C, which is also reinforced from TGA results using a temperature heating rate of 10°C/min [47]. While a larger sample of LDPE was analyzed, the total ion current (TIC) abundance for LDPE was much lower than PS. This is likely due to variation in the yield of ions produced from electron ionization (EI) [39] along with a wider degradation profile seen in LDPE.

These comparative results justify the use of waste plastic for this research, as it is shown their degradation temperatures are similar to studies using standard reference materials [10,38,47]. These results also provide suggested pyrolytic temperatures greater than 450°C to ensure decomposition of both LDPE and PS.

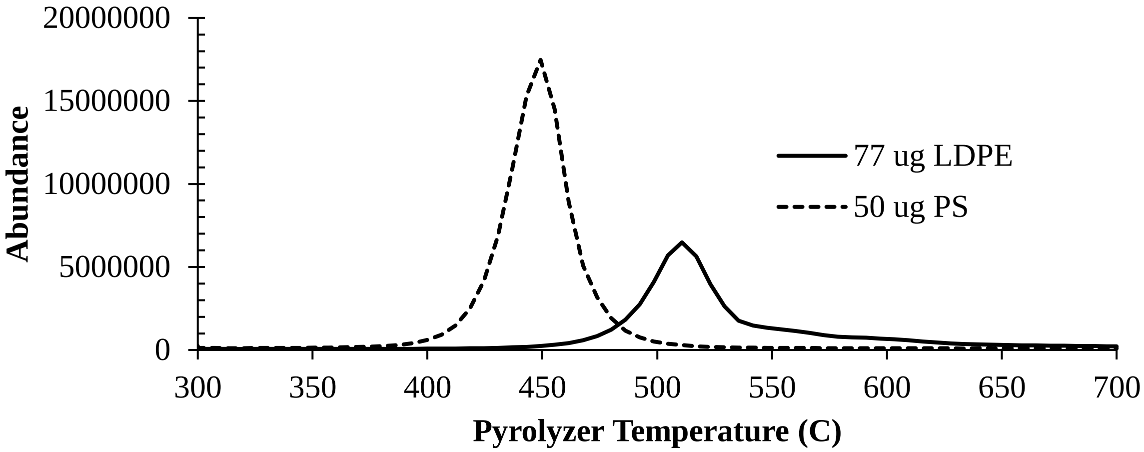

Figure 3-1. EGA-MS TIC thermograms of polystyrene (PS) and low-density polyethylene (LDPE) at a temperature ramp rate of 50°C/min.

3.3.2 Single Plastic Py-GC-MS Analysis

Figure 3-2 contains the total ion current (TIC) of pyrolysis products from low-density polyethylene, with the analyzed hydrocarbons labeled. The range of hydrocarbons observed and identified using the NIST20 library are consistent with polyethylene pyrolysis products reported in the *Pyrolysis-GC-MS Data Book of Synthetic Polymers* [37]. The selected alkenes were analyzed as the twenty most abundant species with the addition of C4 and C39 to expand the range of chain lengths analyzed.

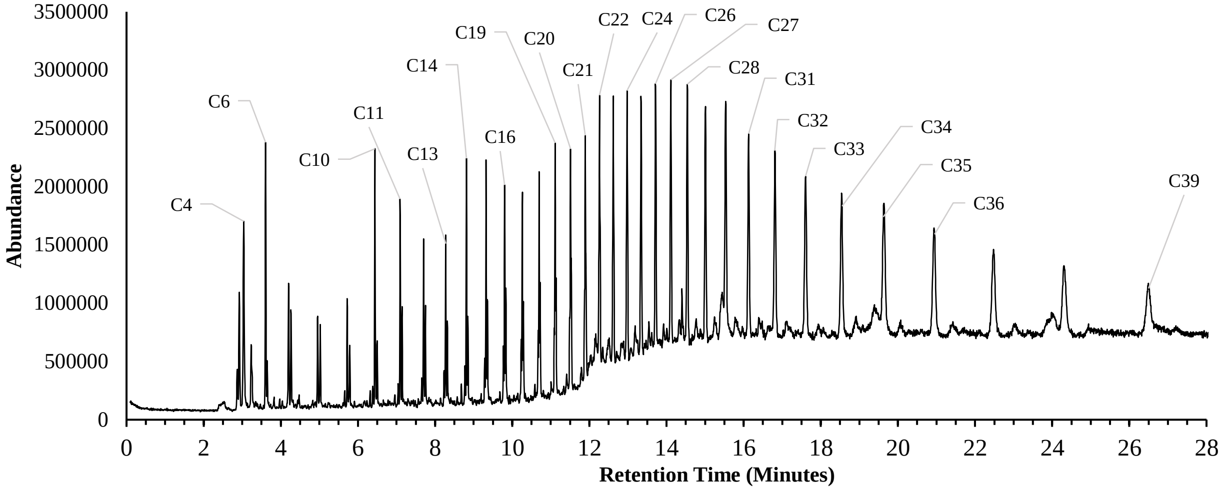

Figure 3-2. Py-GC-MS TIC chromatogram of pyrolysis products of waste low-density polyethylene at 500°C for 30 seconds.

Figure 3-3 shows the three major products identified from polystyrene: toluene, styrene, styrene dimer, and styrene trimer. Consistent with previous work [11,37], these compounds were selected for analysis based on high abundance for integration and comparisons.

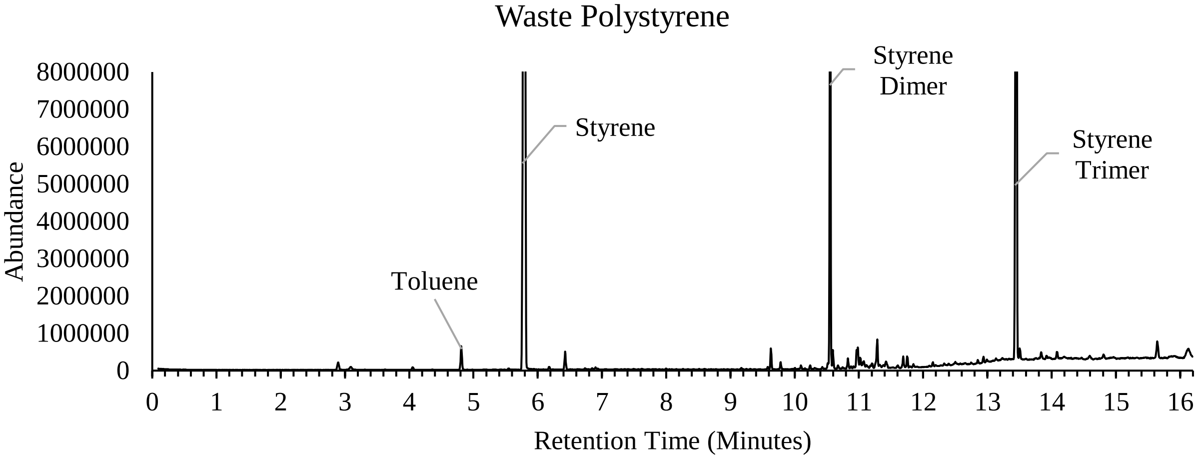

Figure 3-3. Py-GC-MS TIC of pyrolysis products of waste polystyrene at 450°C for 30 seconds.

3.3.3 Binary Polymer Mixture Pyrolysis-GC-MS Analysis

Figure 3-4 shows the major products from low-density polyethylene and polystyrene pyrolysis labeled on the total ion current of 1:1 polystyrene-polyethylene. The coelution of pyrolysis product peaks from polystyrene and low-density polyethylene warrants the need for integration of extracted ions, instead of the total ion current.

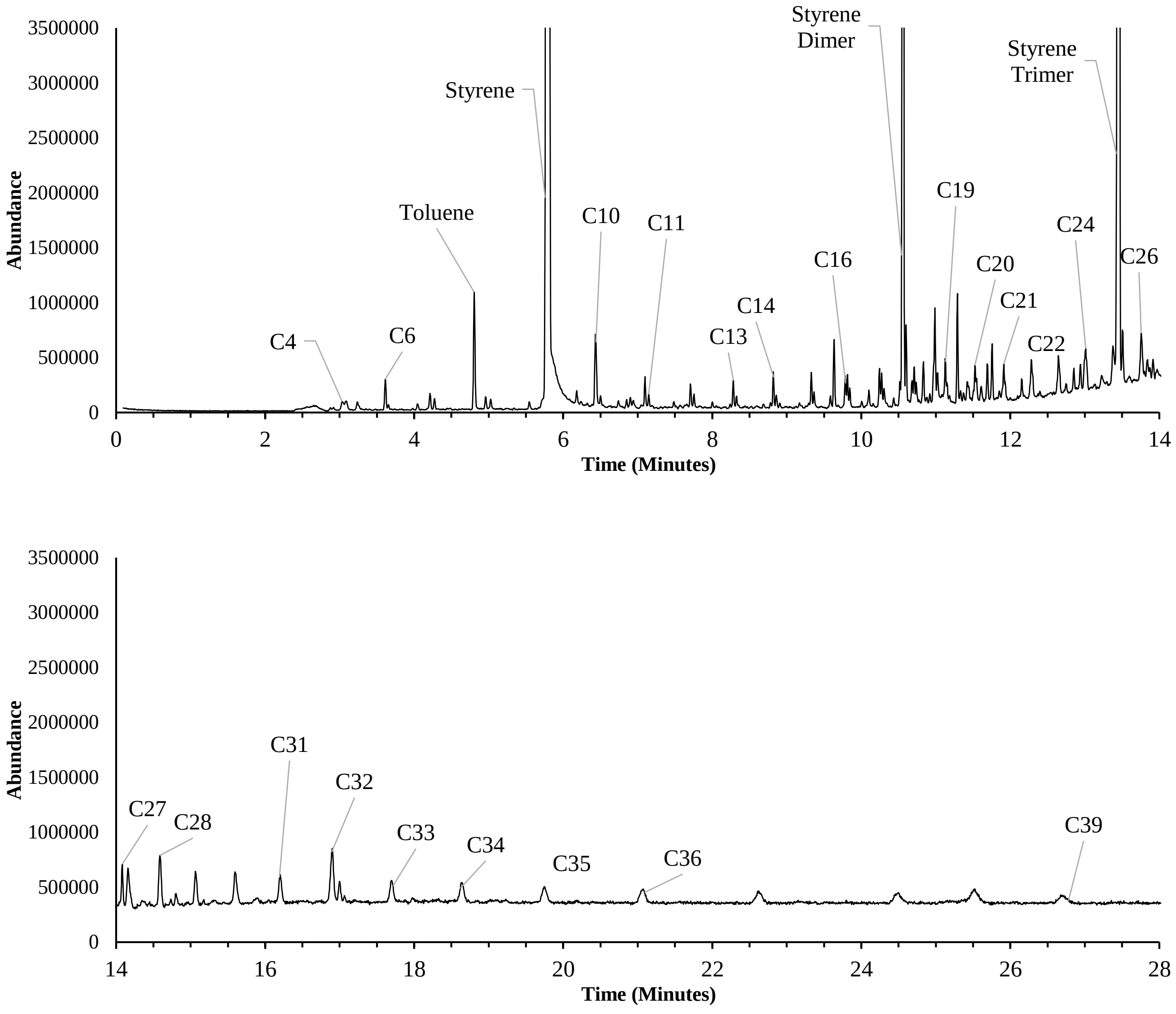

Figure 3-4. Py-GC-MS TIC of pyrolysis products of 1:1 low-density polyethylene-polystyrene at 500°C for 30 seconds.

Table 3-2 Table 3-2. Factorial Regression Results for Analyzed Pyrolysis Productscontains the factorial regression results from the analyzed compounds, with statistically insignificant effects shown in **bold** ($p > 0.05$). With most components having significant effects due to composition, interactions between PS and LDPE products are occurring in a wide range of components. It is also seen that almost all components' relative abundances are affected by temperature.

Table 3-2. Factorial Regression Results for Analyzed Pyrolysis Products

Compound	Composition P-Value	Temperature P-Value	Temperature × Composition Interaction P-Value
C4	0.015	<0.001	0.004
C6	<0.001	<0.001	<0.001
C10	<0.001	<0.001	<0.001
C11	<0.001	<0.001	**0.342**
C13	<0.001	<0.001	<0.001
C14	<0.001	<0.001	0.027
C16	0.164	<0.001	0.198
C19	<0.001	<0.001	0.001
C20	<0.001	0.001	**0.129**
C21	0.002	<0.001	0.001
C22	0.01	**0.493**	<0.001
C24	0.024	<0.001	<0.001
C26	0.015	<0.001	<0.001
C27	**0.516**	<0.001	<0.001
C28	0.088	<0.001	0.001
C31	<0.001	0.001	<0.001
C32	<0.001	0.009	<0.001
C33	<0.001	0.004	**0.959**
C34	<0.001	<0.001	0.092
C35	0.027	0.131	**0.335**
C36	<0.001	<0.001	0.017
C39	**0.147**	<0.001	<0.001
Toluene	<0.001	0.002	0.011
Styrene	<0.001	<0.001	**0.135**
Styrene Dimer	<0.001	0.074	0.052

Styrene Trimer	<0.001	<0.001	**0.124**
*Statistically insignificant effects ($p > 0.05$) **are in bold.**			

Figure 3-5 shows the relative area of LDPE-derived products up to C22 with changing mass composition. At (b) 500 °C, C6, C10, and C11 appear to have a minimum relative area at 1:1 PS:LDPE. This may be due to adduct formation at high volumes of polystyrene or production of aromatics from these chain hydrocarbons. Generally, an increase in PS fraction shows an increase in hydrocarbons shorter than C16, reinforcing previous work by Williams and Williams that polystyrene increases light gas production [13].

Figure 3-6 shows the relative area of LDPE-derived products from C24-C39 with varying feedstock composition. An increase in in C24-C28 at (b) 500 and (c) 550°C with PS fraction increasing, where the opposite is seen at (a) 450°C – indicating an interaction between temperature and composition effecting the relative area of these components. Maximum relative areas for C31-C34 at a mass ratio of 1:1 is shown at (b) 500°C and (c) 500°C. This trend is shown at (a) 450°C as well; however, the variation in these runs makes it hard to statistically distinguish. Much of the heavy-end hydrocarbons produced from polyethylene have not been analyzed or studied in previous work.

These trends are also validated by the p-values presented in **Table 3-2** ($p < 0.05$). This shows that the increase in polystyrene in LDPE-PS mixtures provides more fuel-range hydrocarbons suitable for gasoline or diesel fuels, while decreasing the relative amount of heavier hydrocarbons that would mostly be unusable.

For changes in feedstock composition, only C16, C27, and C39 were to not be significantly affected ($p > 0.05$, **Table 3-2**). This is likely due to these species not participating in secondary reactions at all temperatures.

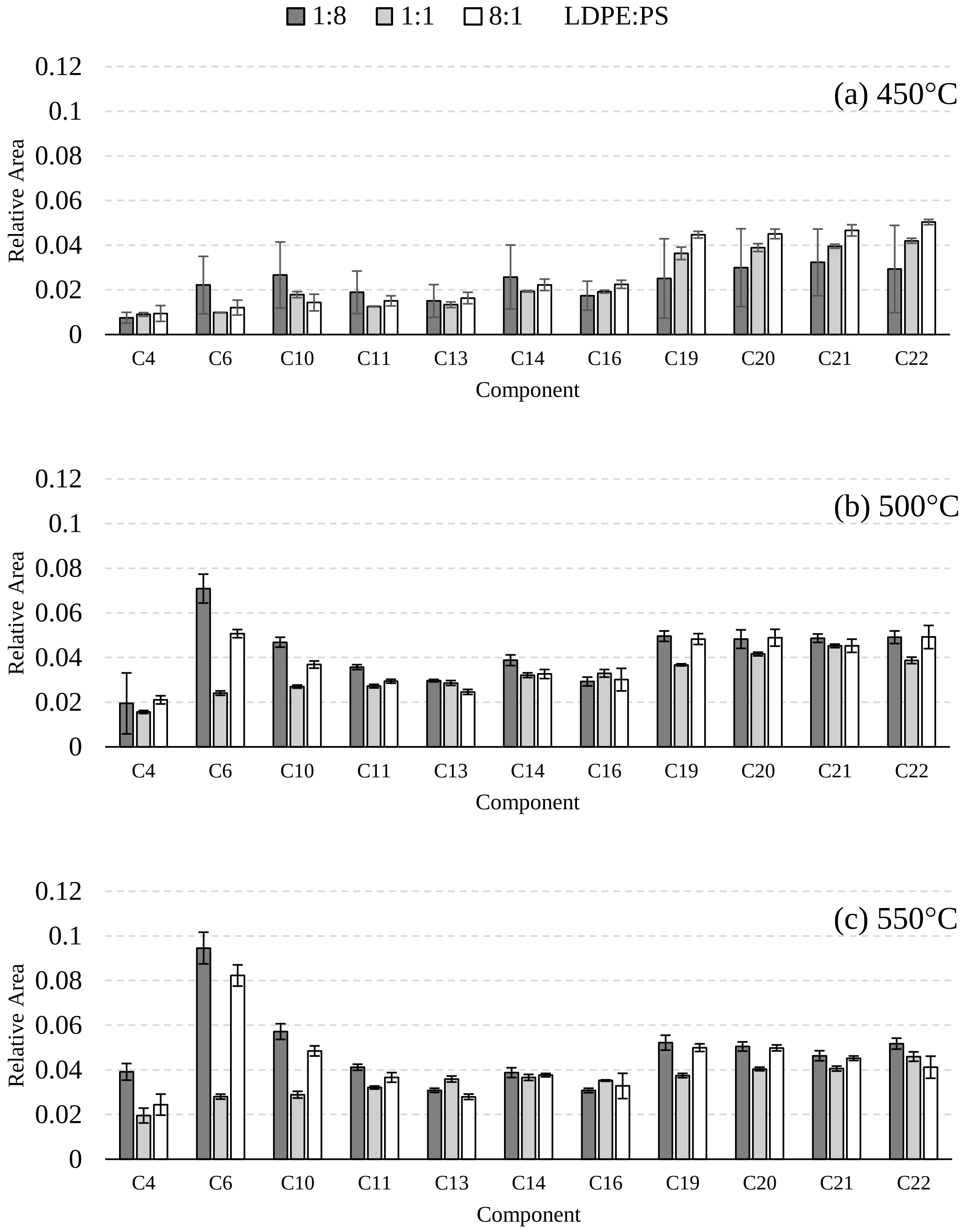

Figure 3-5. Relative extracted ion peak areas of polyethylene products C4-C22 from pyrolysis of low-density polyethylene-polystyrene mixtures with feedstock mass ratios of 1:8, 1:1, and 8:1 at temperatures of (a) 450°C (b) 500°C (c) 550°C.

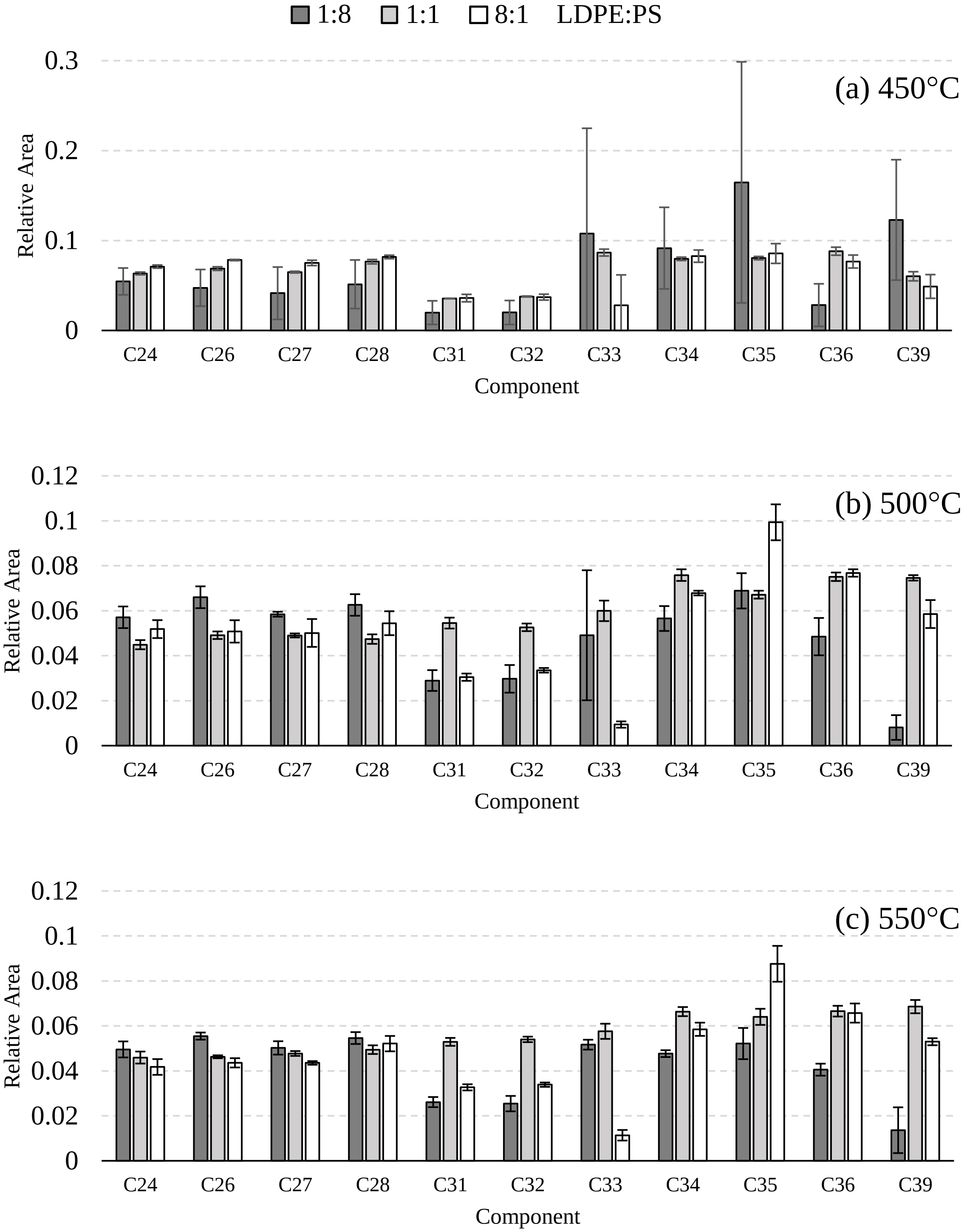

Figure 3-6. Relative extracted ion peak areas of polyethylene products C24-C39 from pyrolysis of low-density polyethylene-polystyrene mixtures with feedstock mass ratios of 1:8, 1:1, and 8:1 at temperatures of (a) 450°C (b) 500°C (c) 550°C.

With varying feedstock composition, increased production of styrene was observed across the temperatures tested **Figure 3-7**. The relative amount of styrene increased with increasing polyethylene mass fraction, whereas the styrene dimer, trimer, and toluene all decreased with increasing polyethylene. These relations are shown to be statistically significant ($p < 0.05$) in **Table 3-2**. This trend is not previously reported in mixture analysis [27,48]. This increased styrene production would provide higher octane ratings for fuels produced from mixed plastic waste along with improving styrene yield to be purified to produce new polystyrene.

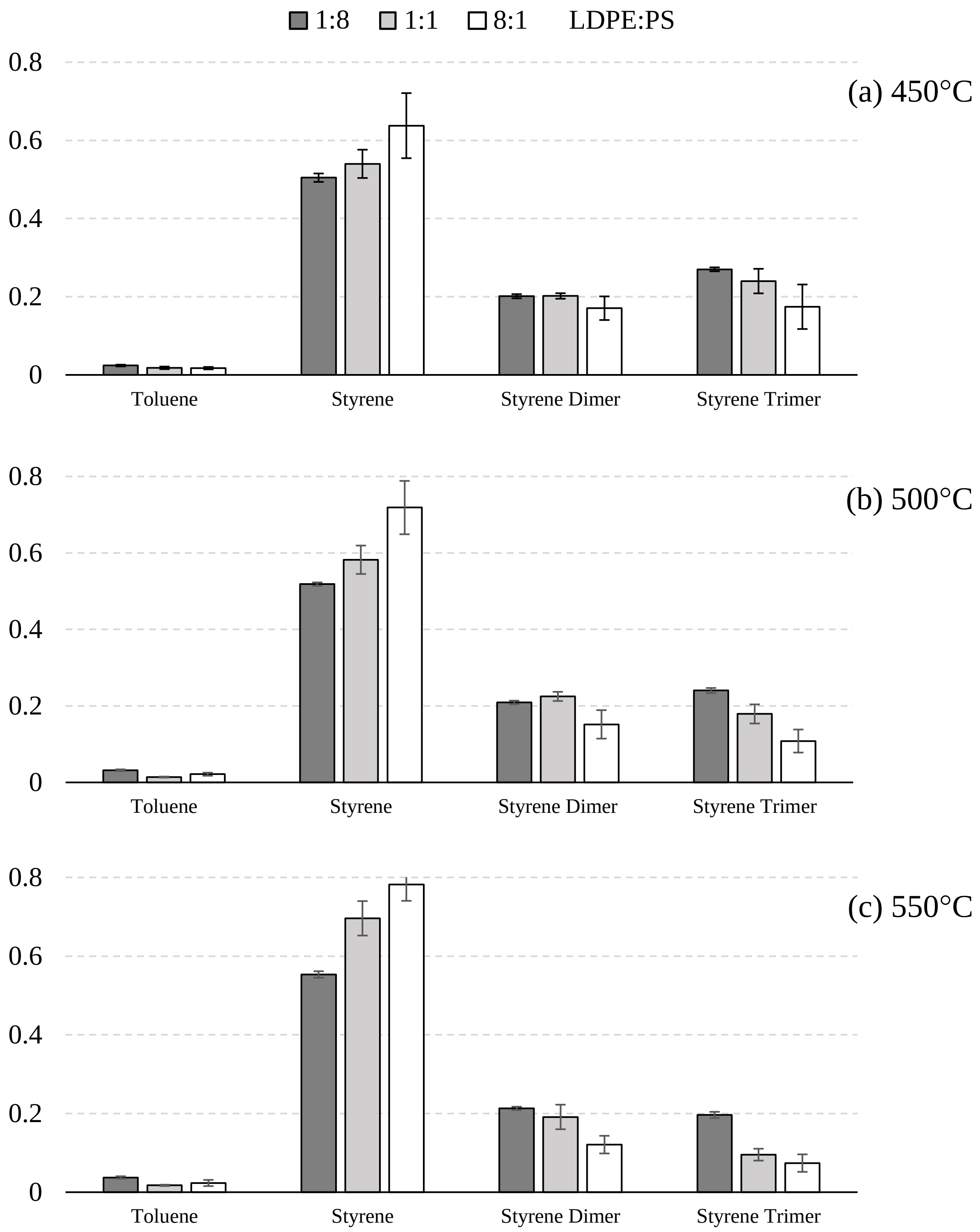

Figure 3-7. Relative extracted ion peak areas of polystyrene products from pyrolysis of low-density polyethylene-polystyrene mixtures with feedstock mass ratios of 1:8, 1:1, and 8:1 at temperatures of (a) 450°C (b) 500°C (c) 550°C.

Figure 3-8 shows the relative areas of polyethylene products C4-C22 with varying temperatures. In **Figure 3-8a,** an increase in C4 through C22 hydrocarbons are seen for the 1:8 mixture of LDPE:PS, as expected. **Figure 3-8b,c** show an increase in C4-C16 hydrocarbons; however, the C19-C22 hydrocarbons do not increase as much for 1:1 and 8:1 LDPE:PS. This may be due to the promotion of decomposition by polystyrene on polyethylene suggested by Williams and Williams [13].

The relative areas of polyethylene products C24-C39 are shown in **Figure 3-9** with varying temperatures. **Figure 3-9a** shows a maximum relative area for C24-C32 across the range of 450-550°C, with a decrease in relative area with temperature increasing for C33-C36. C39 appears to have a minimum in this temperature range in the 1:8 mixture as well. In both **Figure 3-9a and b**, with respect to temperature, C24-C28 decrease, C31-C32 increase, C33-C36 decrease, and a maximum is seen around 500°C for C39 for 1:1 and 8:1 LDPE:PS mixtures. Decreasing heavier hydrocarbons is expected as pyrolytic temperatures increase, resulting in higher relative amounts of lighter products; however, the maximum seen in C39 would indicate breakdown of heavier products that are not analyzed by the GC-MS.

A general increase in light fuel-range hydrocarbons with increasing temperature reinforced statistically ($p < 0.05$, **Table 3-2**) along with decreasing amounts of heavier hydrocarbons, optimal pyrolytic temperatures for production of fuels would be in the higher range between 500-550°C to limit excess production of light gases (C4).

For temperature, only C22 and C35 are seen as not being significantly affected ($p > 0.05$). It is likely that the temperature range studied resulted in an increased production of these oligomers, but higher temperatures also increased the decomposition of the species to yield lighter compounds.

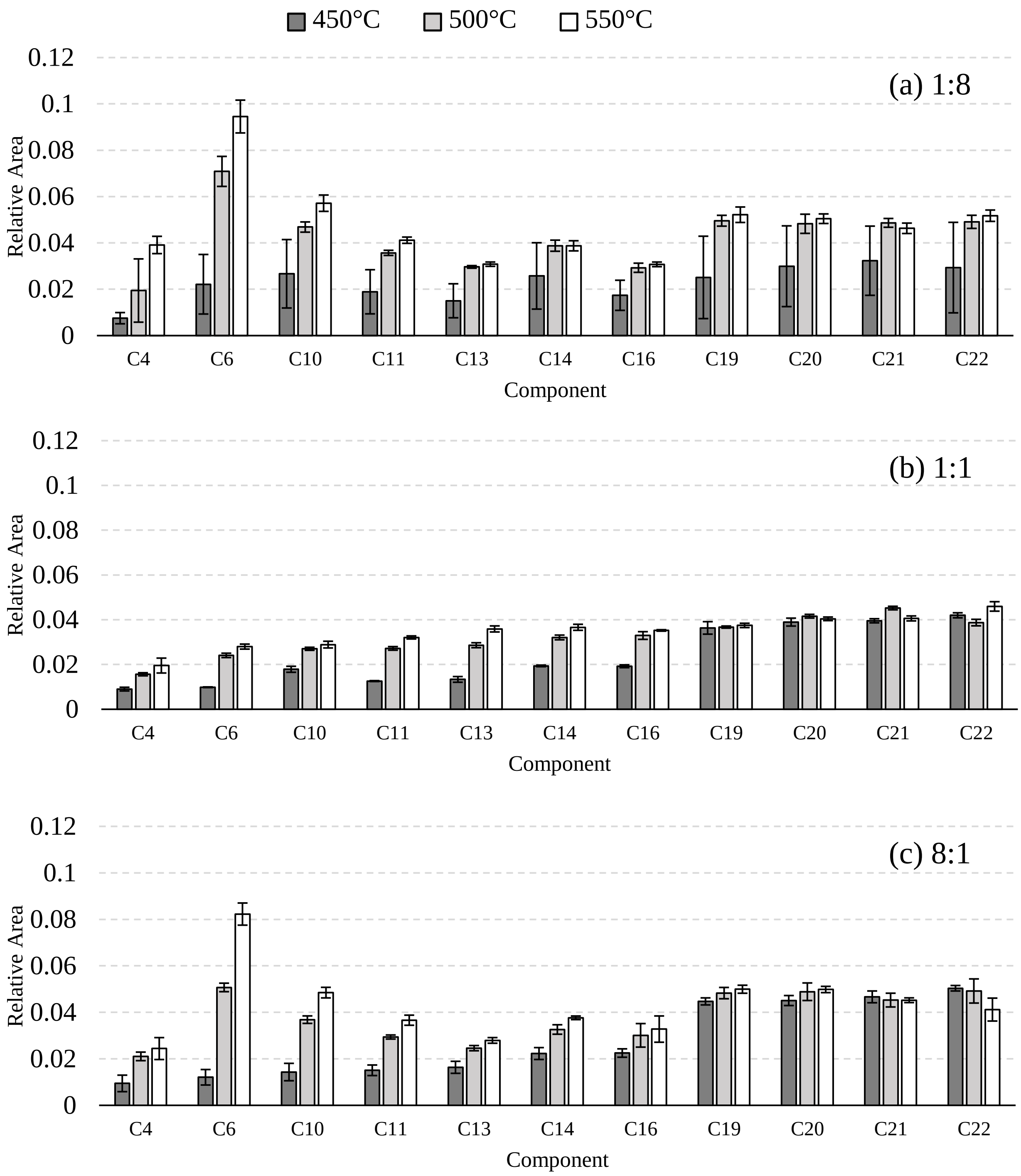

Figure 3-8. Relative extracted ion peak areas of polyethylene products C4-C22 from pyrolysis of low-density polyethylene-polystyrene mixtures at temperatures of 450°C, 500°C, and 550°C with feedstock mass ratios of (a) 1:8, (b) 1:1, and (c) 8:1.

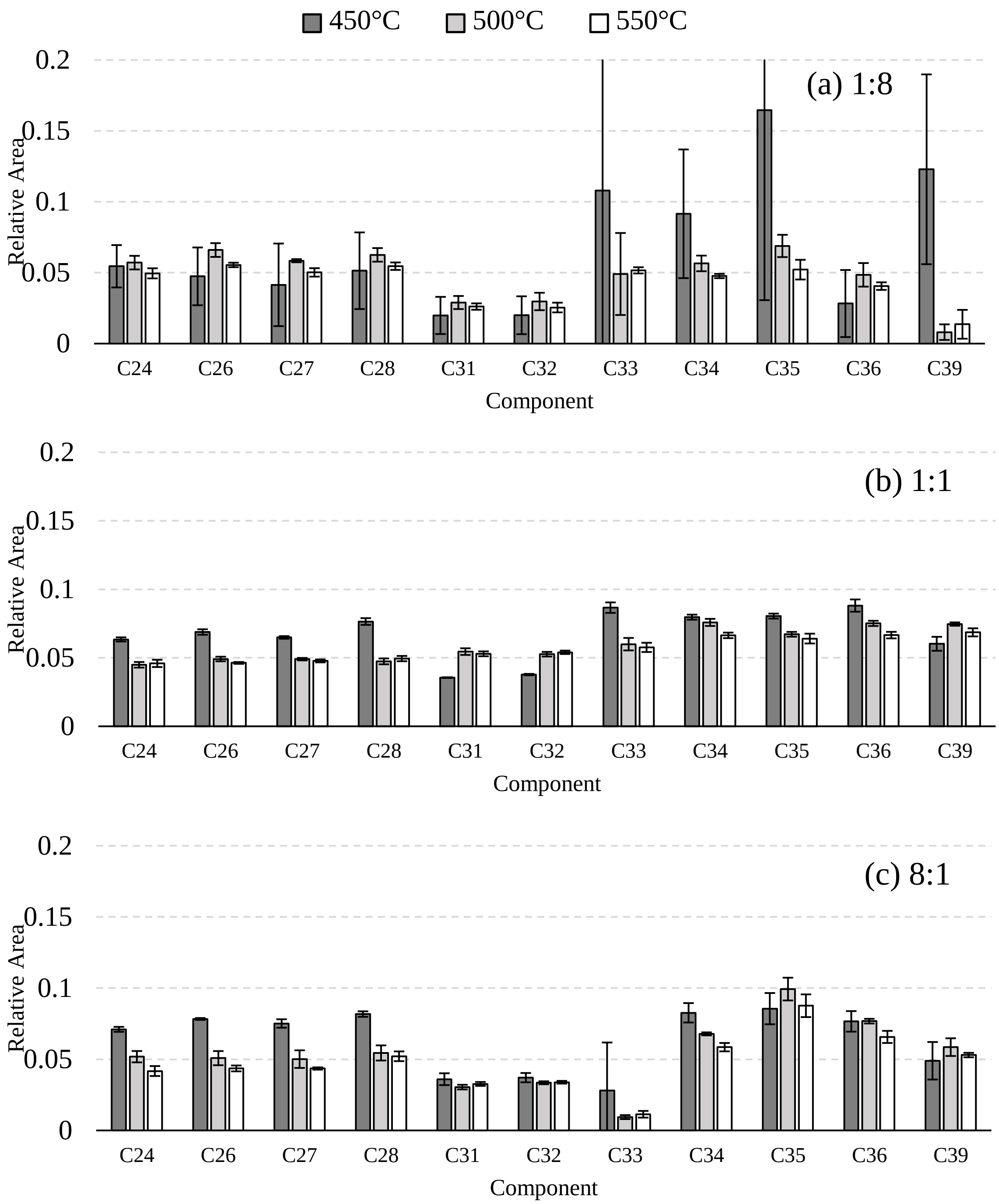

Figure 3-9. Relative extracted ion peak areas of polyethylene products C24-C39 from pyrolysis of low-density polyethylene-polystyrene mixtures at temperatures of 450°C, 500°C, and 550°C with feedstock mass ratios of (a) 1:8, (b) 1:1, and (c) 8:1.

Figure 3-10 shows the relative areas of styrene products with varying temperature at each compositional level. With increasing temperature, styrene and toluene increase in yield with a decrease in the styrene trimer ($p < 0.05$), likely as products degrade further – as previously reported [32]. Interestingly, the styrene dimer does not change greatly with temperature ($p > 0.05$), likely since it is a product of the degradation of the trimer, but also breaks down further to produce styrene. With increasing yields in styrene, pyrolysis of mixtures to produce monomers for new plastics would be best at 550°C in the range studied.

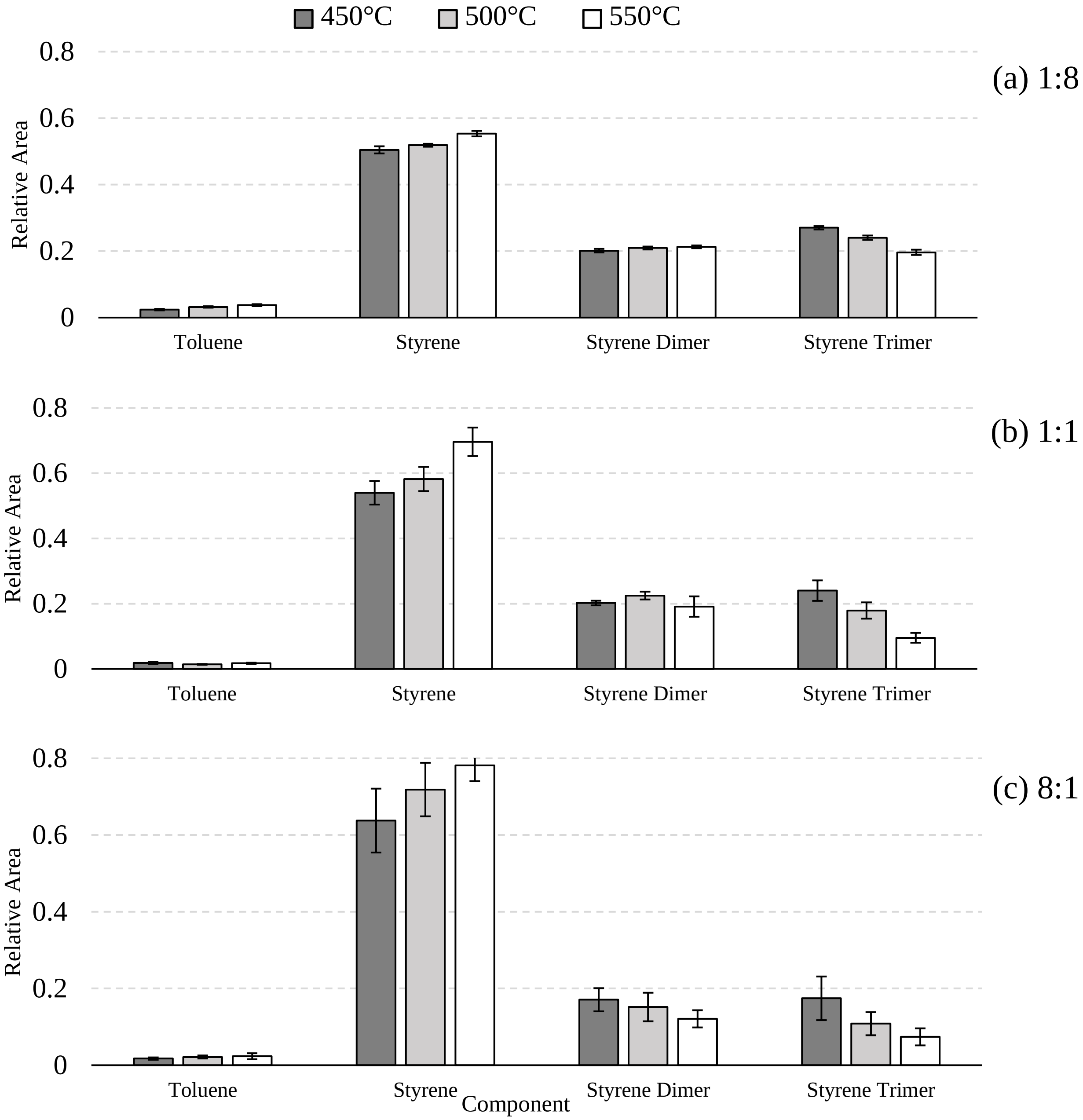

Figure 3-10. Relative extracted ion peak areas of polystyrene products from pyrolysis of low-density polyethylene-polystyrene mixtures at temperatures of 450°C, 500°C, and 550°C with feedstock mass ratios of (a) 1:8, (b) 1:1, and (c) 8:1.

3.3.4 Implications for Application

With mixed polystyrene and low-density polyethylene, the major focus is the amount of fuel-range olefins and the amount of styrene produced to be used to produce new plastic. This work has shown that increasing the amount of polystyrene relative to polyethylene results in an increased breakdown of polyethylene. This is important to allow for lower temperatures to produce higher fractions of liquid and gaseous fuel. At a lower temperature, the energy requirements to heat and pyrolyze the plastic will be significantly reduced. In the same point, an increased amount of polyethylene relative to polystyrene increases the production of styrene as a monomer for new plastics. This work shows that mixtures of plastic can result in advantageous interactions for the application of fuel production and monomers for new plastics.

3.4 Conclusions

In this study, the fast pyrolysis of waste polystyrene and low-density polyethylene were studied using Pyrolysis-GC-MS at temperatures of 450, 500, and 550°C for 30 seconds. It was determined that there was significant impact of temperature on product composition for the binary mixtures of polyethylene and polystyrene, as expected [18–20,36,40].

Feedstock composition only had a significant impact on product composition except for C16, C27, and C39 produced from polyethylene, suggesting all other products are affected by secondary reactions between plastic species. This is not previously reported, likely due to limited compositional ranges studied in by Coralli et al. 2022 and Williams and Williams 1999 [13,27]. The impact of polystyrene increasing production of light gases by approximately 50% was expected as previously reported [13]. Future work should further investigate similar composition at higher temperatures to investigate the combined effect of temperature and composition on product distribution to produce fuels and commodity chemicals.

4 Chapter IV: Conclusions and Recommendations

Overall, this work concluded that there are interactions between homopolymer polyolefins – polypropylene and low-density polyethylene – and polystyrene when co-pyrolyzed. Increased production of light gases with increase in polystyrene has been seen in previous work [13]; however, the effects seen impacting production of fuel-range hydrocarbons were not.

While this work has provided insight towards secondary reactions between plastic species, it has been limited to relative areas produced by ion response from the mass spectrometer. Other work on single plastic species has made use of Pyrolysis-GC-MS-FID with a total methanizer to allow for mass fraction calculations from flame-ionization detector (FID) response in conjunction with mass spectral identification [26]. Using this technique, quantitative analysis of products can be conducted.

This work has provided identification and qualitative analysis of a variety of compounds produced from complete pyrolysis of the selected plastic types at varying temperatures and compositions. These compounds can be used for analysis of shorter experiments to allow for the development of kinetic models including interactions between plastic species that was described in this work.

The effects of temperature on pyrolysis products were analyzed within the range of 450 – 550°C and showed improved yields of fuel-range hydrocarbons and reducing yield of larger waxy compounds. With the development of bench-top and pilot-scale fluidized bed reactors in the group, Pyrolysis-GC-MS of resultant oils to analyze the benefit of a secondary pyrolysis reactor to further breakdown initial products would provide insight towards large-scale applications.

5 References

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A. APPENDIX A: Py-GC-MS Experiments

A.1 GC-MS Acquisition Parameters

```
INSTRUMENT CONTROL PARAMETERS:    GCMS 7890
                ------------------------------------------

   D:\METHODS\Zach\22_0523_S50_16LONG_Punion_MS.M
      Tue Jun 21 10:04:50 2022

Control Information
------- -----------

Sample Inlet            : GC
Injection Source        : Manual
Mass Spectrometer       : Enabled


 No Sample Prep method has been assigned to this method.


GC
GC Summary
Run Time                            28.2 min
Post Run Time                          0 min

Oven
Temperature
Setpoint                          On
(Initial)                       40 °C
Hold Time                          1 min
Post Run                         40 °C
Program
#1 Rate                           25 °C/min
#1 Value                           320 °C
#1 Hold Time                          0 min
#2 Rate                           25 °C/min
#2 Value                           320 °C
#2 Hold Time                          16 min

Equilibration Time                     1 min
Max Temperature                       325 °C
Maximum Temperature Override              Disabled
Slow Fan                               Disabled
Cryo                                 Off
```

```
Cryo Type                      N2

Front MM Inlet He
Front MM Inlet He Temperature
Setpoint                     Off
(Initial)                  250 °C

Excluded from Readiness                ***Excluded from Affecting GC's Readiness
State***
Mode                         Split
Pressure                     Off
Total Flow                     Off
Septum Purge Flow                   Off
Cryo                        Off
Cryo Type                      N2

Back SS Inlet He
Mode                         Split
Heater                      On    300 °C
Pressure                     On    13.441 psi
Total Flow                     On    53.133 mL/min
Septum Purge Flow                   On    3 mL/min
Gas Saver                      Off
Split Ratio                   50 :1
Split Flow                     49.15 mL/min

Thermal Aux 1 (MSD Transfer Line)
Temperature
Setpoint                     On
(Initial)                  300 °C


Thermal Aux 2 (User Configurable)
Temperature
Setpoint                     Off
(Initial)                  450 °C


Column
Column #1
Flow
Setpoint                     On
(Initial)                  0.98301 mL/min
Post Run                      1 mL/min

Column Information                   Frontier xxxx
```

```
Description                     with union
Temperature Range                   -60 °C—360 °C (380 °C)
Dimensions                       51 m x 250 µm x 0.25 µm (Calibrated)
Heater                         Oven
In                           Back SS Inlet He
Out                           MSD
(Initial)                     40 °C
Pressure                        13.441 psi
Flow                          0.98301 mL/min
Average Velocity                   27.574 cm/sec
Holdup Time                     3.0826 min
Control Mode                    Constant Flow


MS Information
-- -----------



General Information
------- -----------



Acquisition Mode         : Scan
Solvent Delay (minutes)  : 0
Tune file               : D:\MassHunter\GCMS\1\5975\atune.u
EM Setting mode Delta    : 0.000000

Normal or Fast Scanning  : Normal Scanning
Trace Ion Detection      : Off
Run Time (if MS only)    : 650 minutes

[Scan Parameters]
Start Time              : 0
Low Mass                  : 10
High Mass                 : 550
Threshold               : 150
A/D Samples:              : 4


[MSZones]

MS Source                  : 230 C   maximum 250 C
MS Quad                    : 150 C   maximum 200 C

Timed Events
----- ------
```

```
Number Events= 0


                END OF MS ACQUISITION PARAMETERS


                  TUNE PARAMETERS for SN: US10739010
                  --------------------------------

 Trace Ion Detection is OFF.

   34.610   :   EMISSION
   70.347   :   ENERGY
   34.961   :   REPELLER
   88.259   :   IONFOCUS
   22.000   :   ENTRANCE_LENS
 2082.353   :   EMVOLTS
                       2082.353  : Actual EMV
                          6.39   : GAIN FACTOR
 1461.000   :   AMUGAIN
  126.250   :   AMUOFFSET
    2.000   :   FILAMENT
    0.000   :   DCPOLARITY
   21.082   :   ENTLENSOFFSET
 -987.000   :  MASSGAIN
  -39.000   :  MASSOFFSET

                  END OF TUNE PARAMETERS
                  ----------------------



                 END OF INSTRUMENT CONTROL PARAMETERS
                 -----------------------------------
```

A.2 LDPE:PS Mixture Experiments

Table A-1. Components Identified in LDPE-PS Experiments

Compound	**Target Ion (*m/z*)**	**Plastic Produced From**	**Retention Time (min)**
C4	56	**LDPE**	3.033
C6	56	**LDPE**	3.617
C10	55	**LDPE**	6.439
C11	55	**LDPE**	7.097
C13	55	**LDPE**	8.284
C14	55	**LDPE**	8.819
C16	55	**LDPE**	9.815
C19	55	**LDPE**	11.125
C20	55	**LDPE**	11.524
C21	55	**LDPE**	11.912
C22	55	**LDPE**	12.287
C24	55	**LDPE**	13.024
C26	55	**LDPE**	13.768
C27	55	**LDPE**	14.162
C28	55	**LDPE**	14.598
C31	97	**LDPE**	16.197
C32	97	**LDPE**	16.892
C33	57	**LDPE**	17.187
C34	57	**LDPE**	17.697
C35	57	**LDPE**	19.757
C36	57	**LDPE**	21.079
C39	57	**LDPE**	26.73
Toluene	91	*PS*	4.804
Styrene	104	*PS*	5.795
Styrene Dimer	91	*PS*	10.559
Styrene Trimer	91	*PS*	13.455

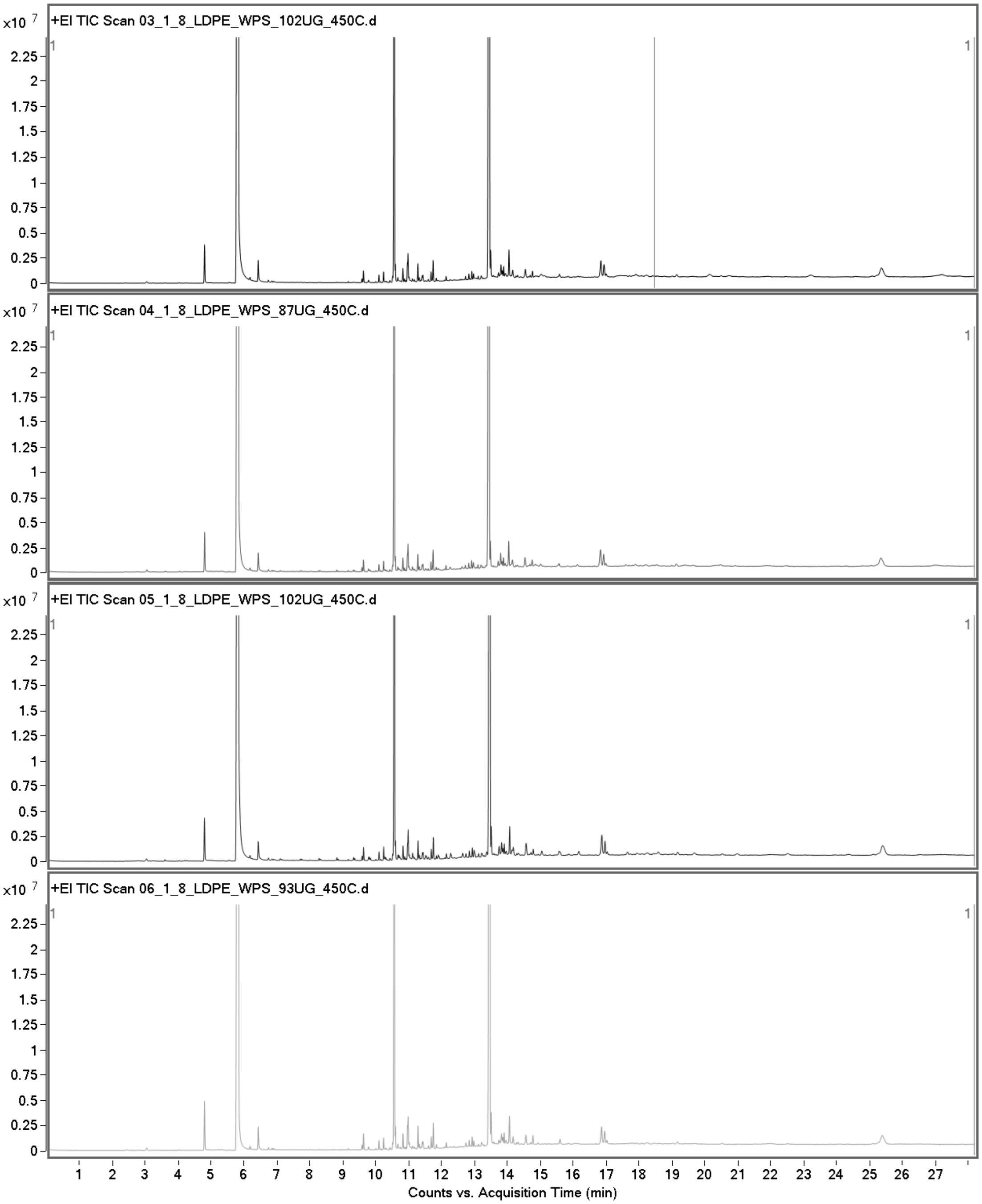


Figure A-1. Total ion current for 30 second 450°C single-shot experiments of 1:8 LDPE:PS.

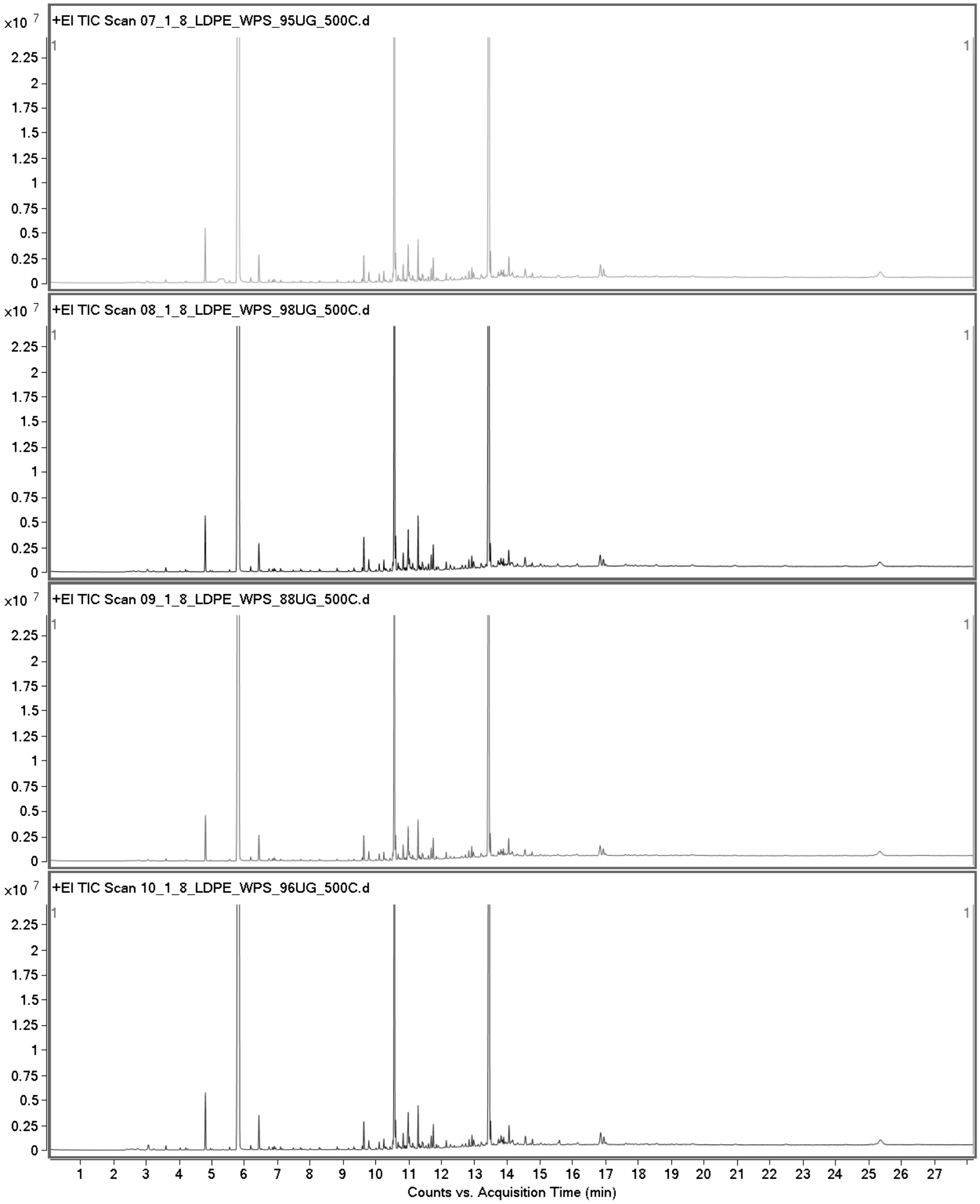


Figure A-2. Total ion current for 30 second 500°C single-shot experiments of 1:8 LDPE:PS.

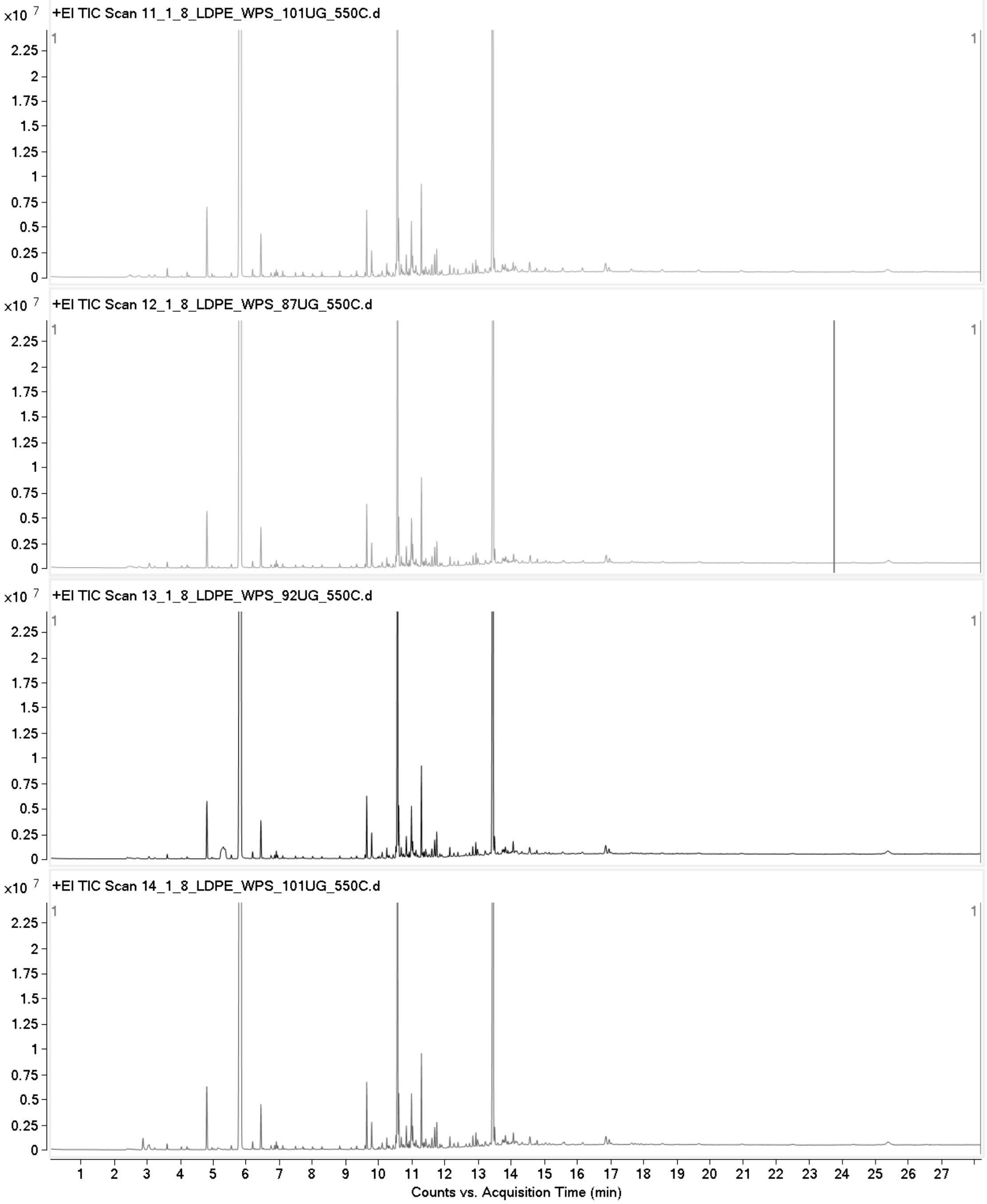


Figure A-3. Total ion current for 30 second 550°C single-shot experiments of 1:8 LDPE:PS.

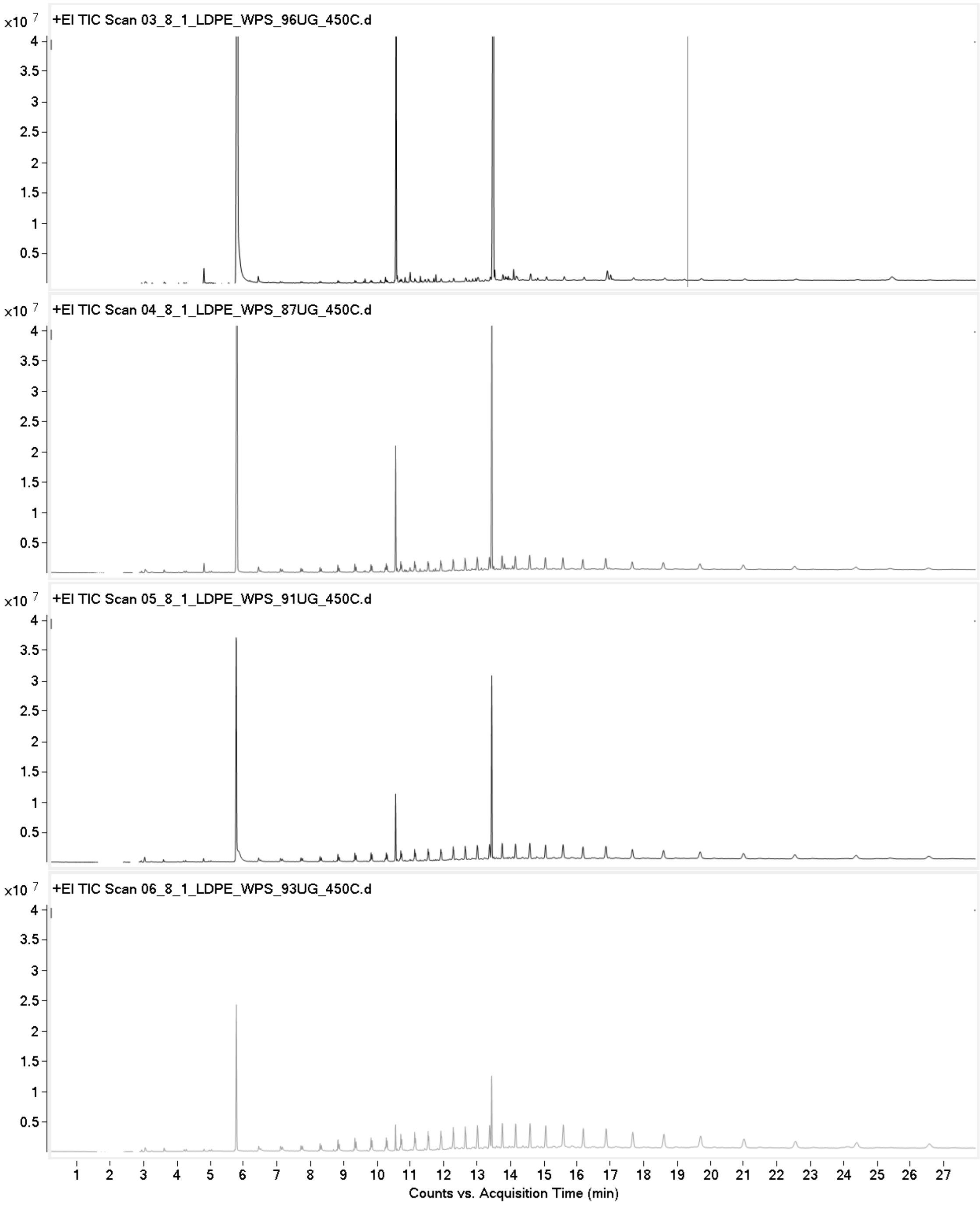


Figure A-4. Total ion current for 30 second 450°C single-shot experiments of 8:1 LDPE:PS.

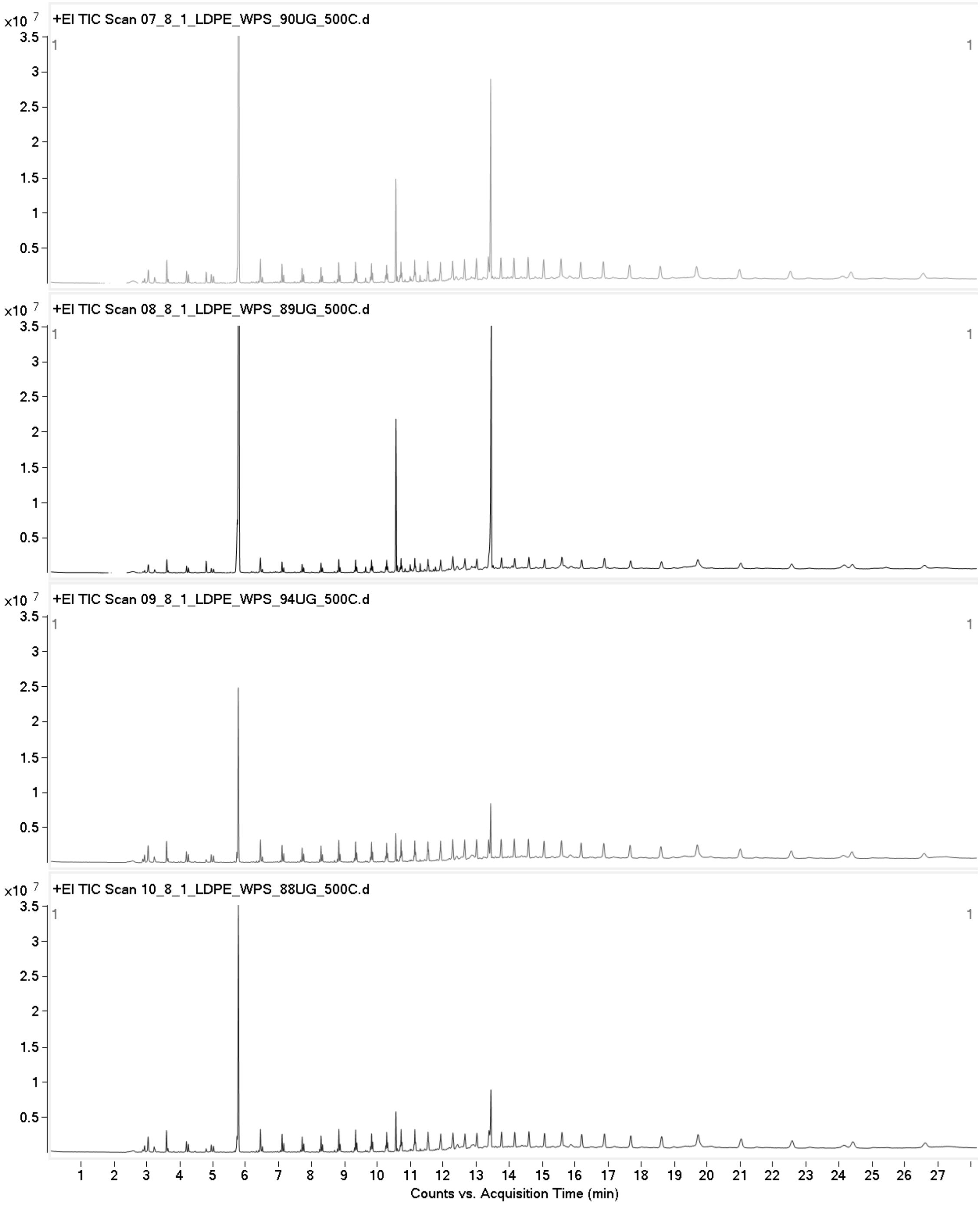


Figure A-5. Total ion current for 30 second 500°C single-shot experiments of 8:1 LDPE:PS.

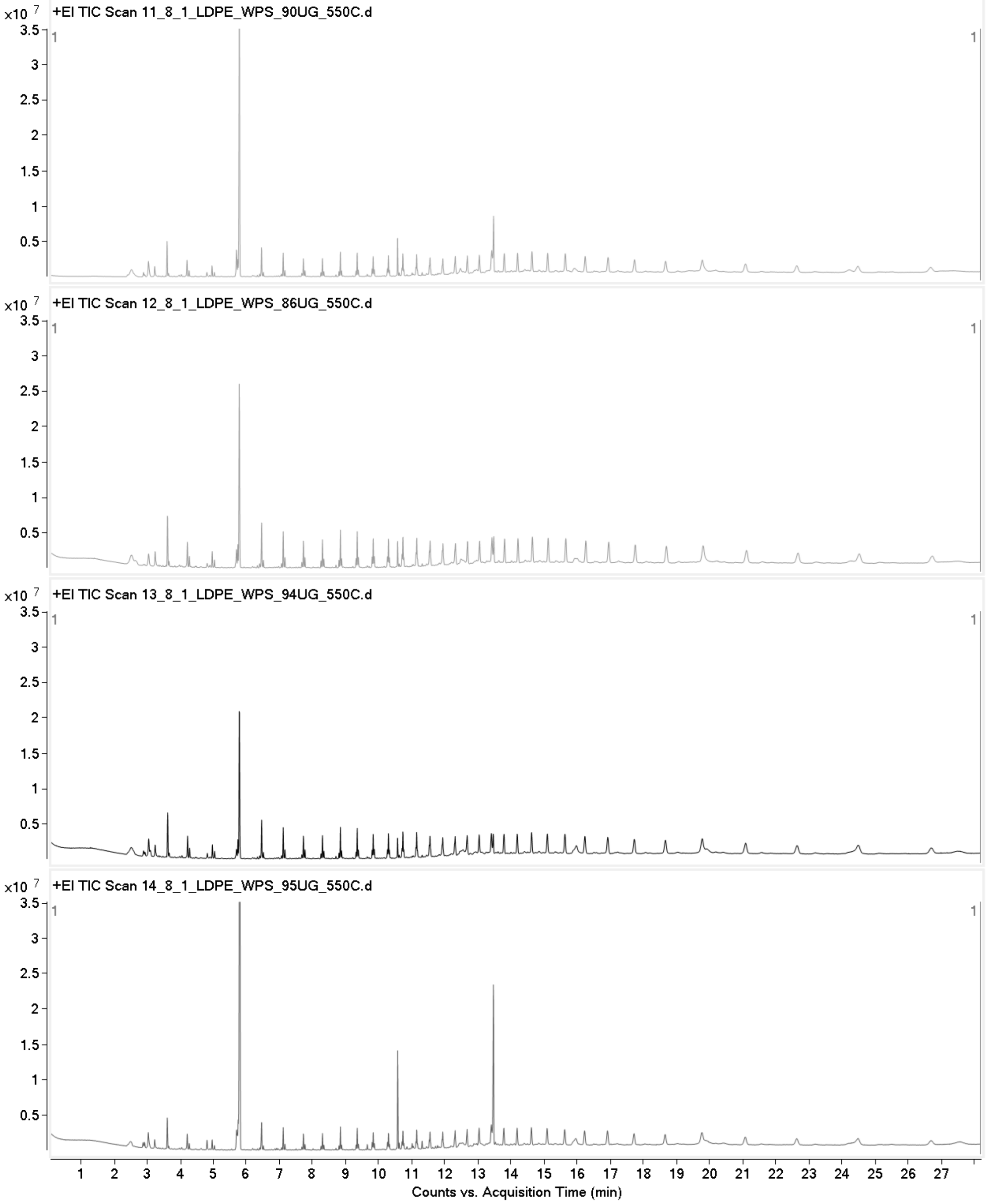


Figure A-6. Total ion current for 30 second 550°C single-shot experiments of 8:1 LDPE:PS.

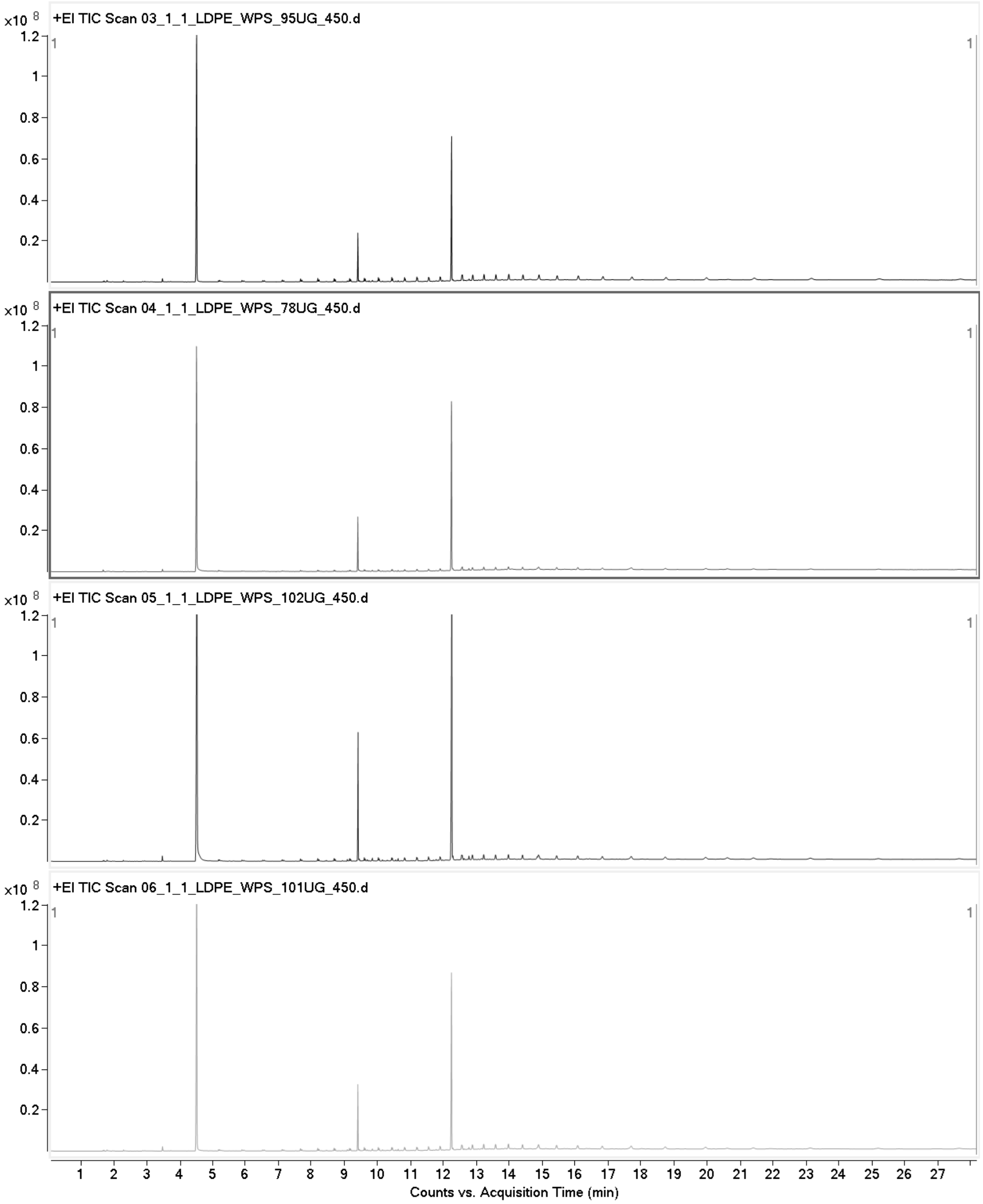


Figure A-7. Total ion current for 30 second 450°C single-shot experiments of 1:1 LDPE:PS.

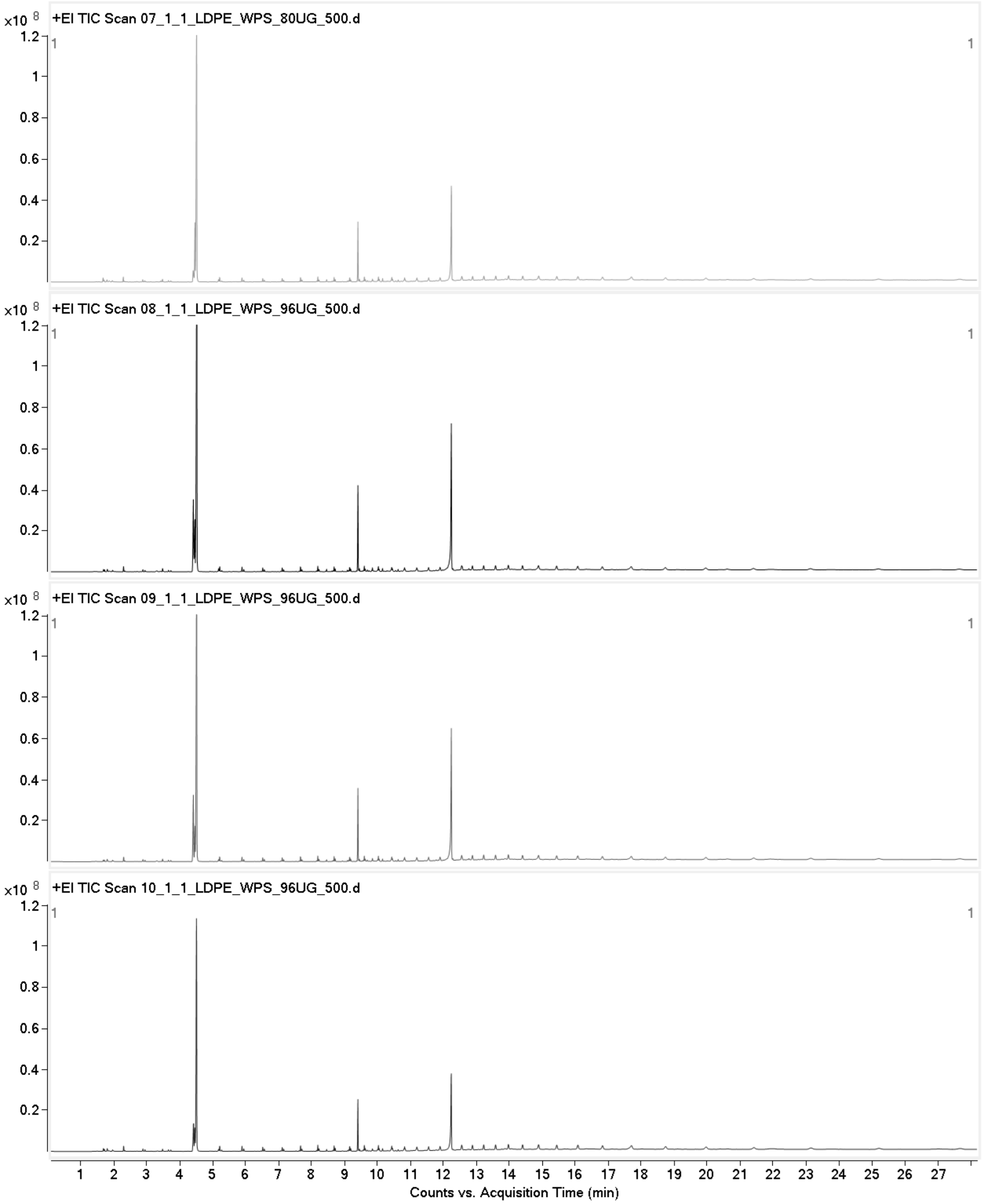


Figure A-8. Total ion current for 30 second 500°C single-shot experiments of 1:1 LDPE:PS.

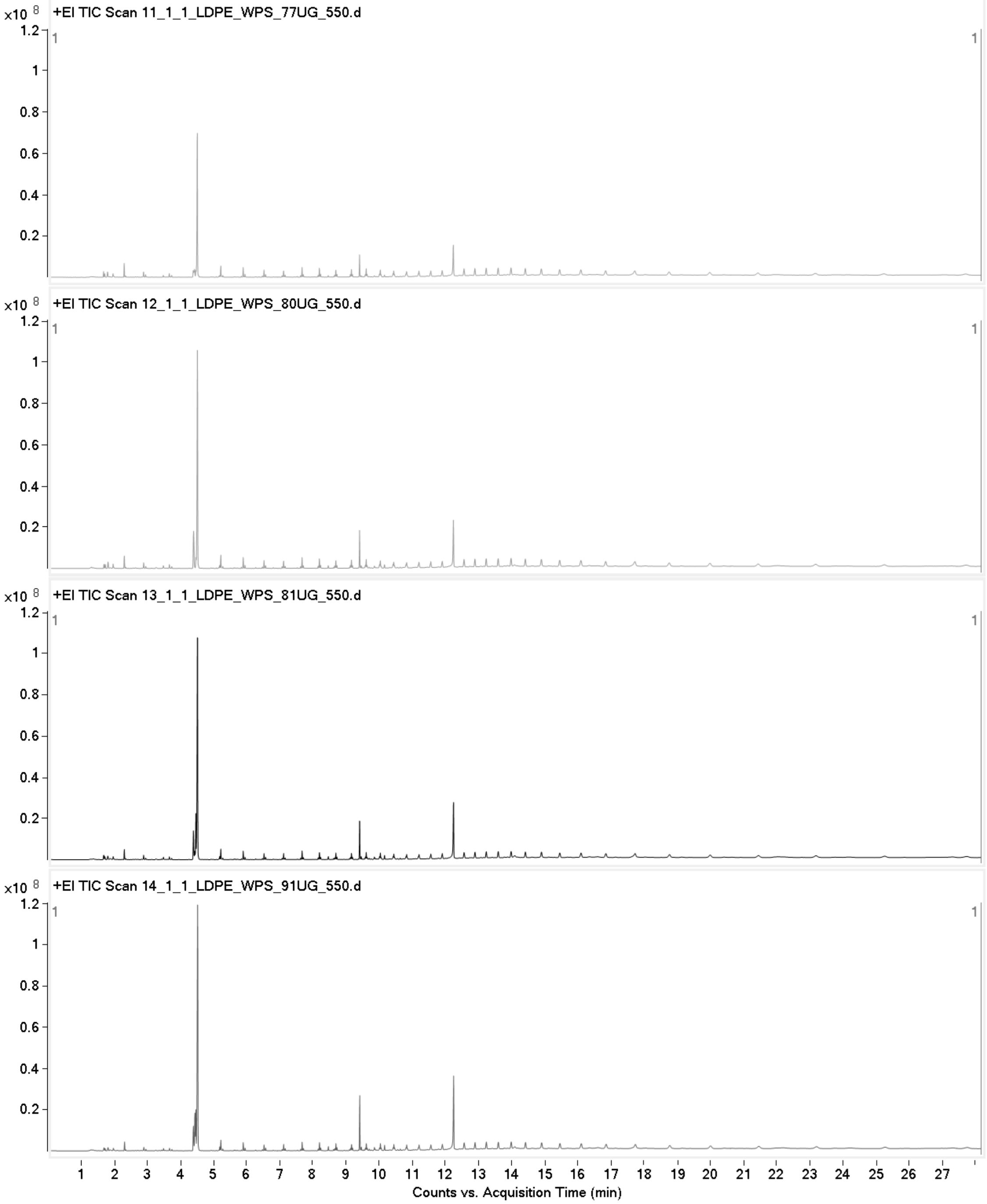


Figure A-9. Total ion current for 30 second 550°C single-shot experiments of 1:1 LDPE:PS.

A.3 PP:PS Experiments

Table A-2. Components Identified in PP-PS Mixture Experiments

Component	**Retention Time (minutes)**	**Base Peak Ion**
PP-C9	4.04	69
PP-C12	5.82	69
PP-C15	7.2	69
PP-C18	8.37	69
PP-C22	9.52	69
Styrene	4.49	104
Styrene Dimer	9.41	91
Styrene Trimer	12.27	91

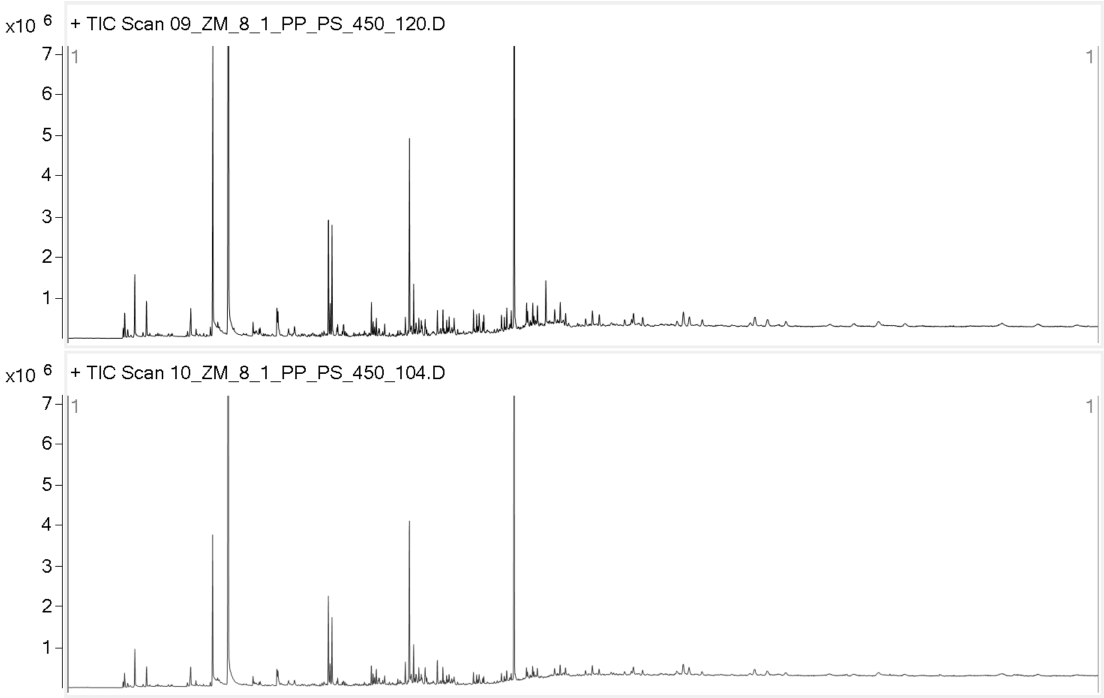


Figure A-10. Total ion current for 30 second 450°C single-shot experiments of 8:1 PP:PS.

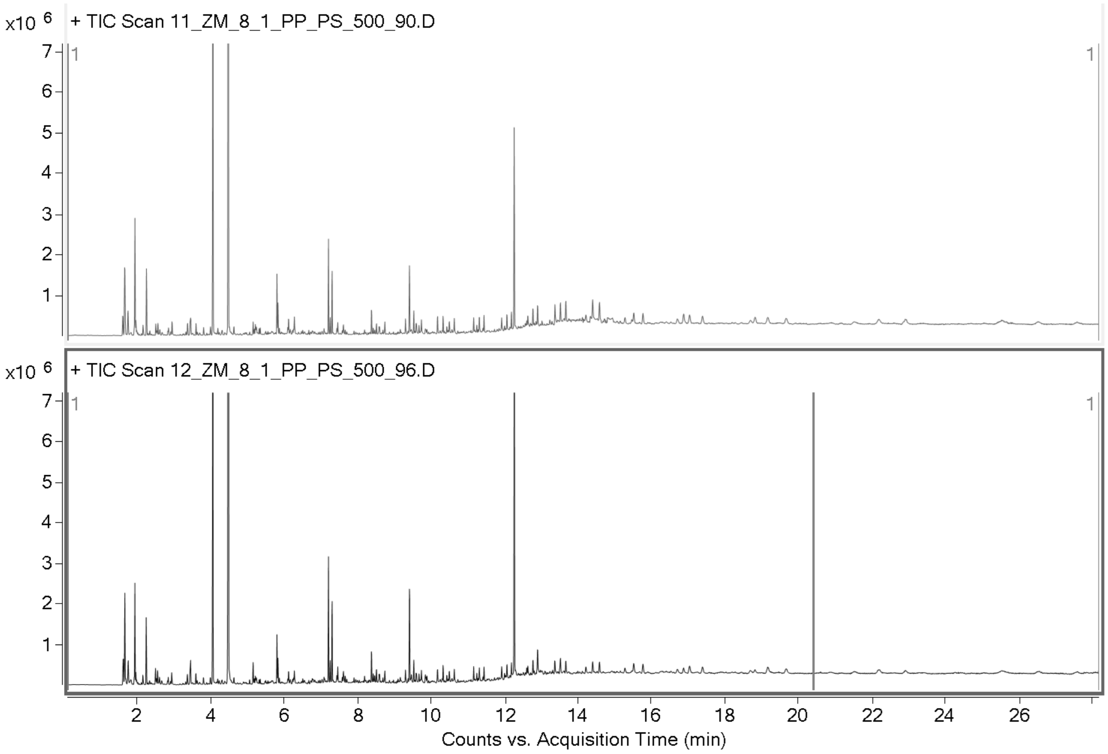


Figure A-11. Total ion current for 30 second 500°C single-shot experiments of 8:1 PP:PS.

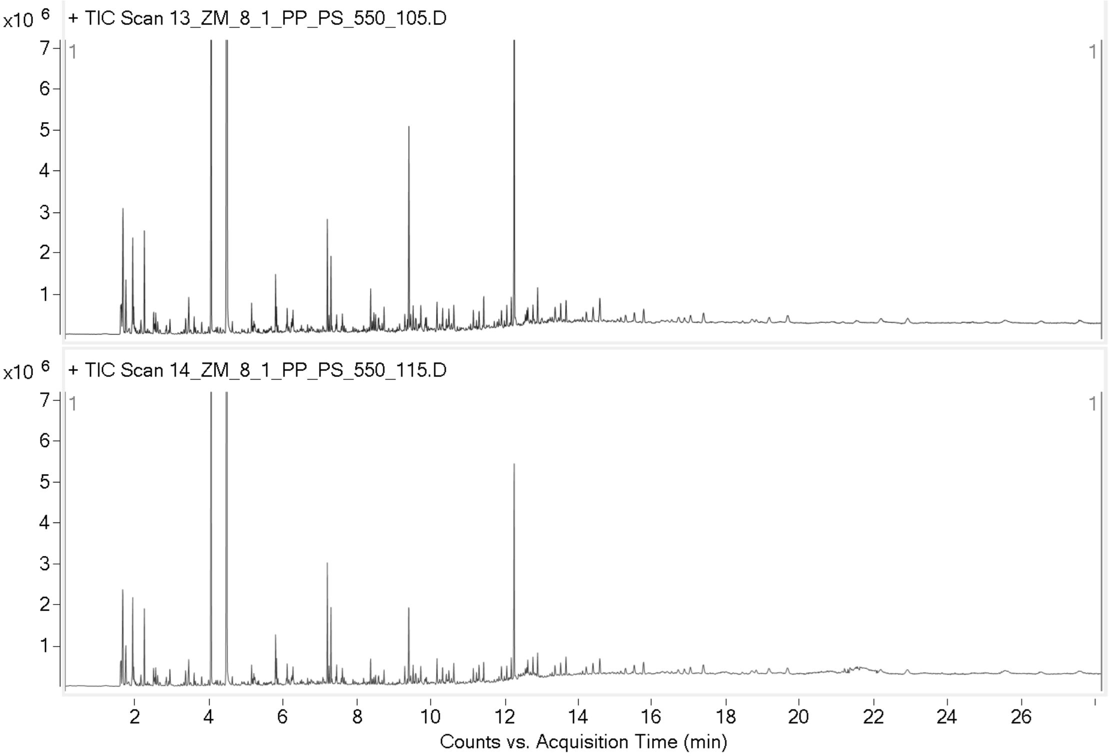


Figure A-12. Total ion current for 30 second 550°C single-shot experiments of 8:1 PP:PS.

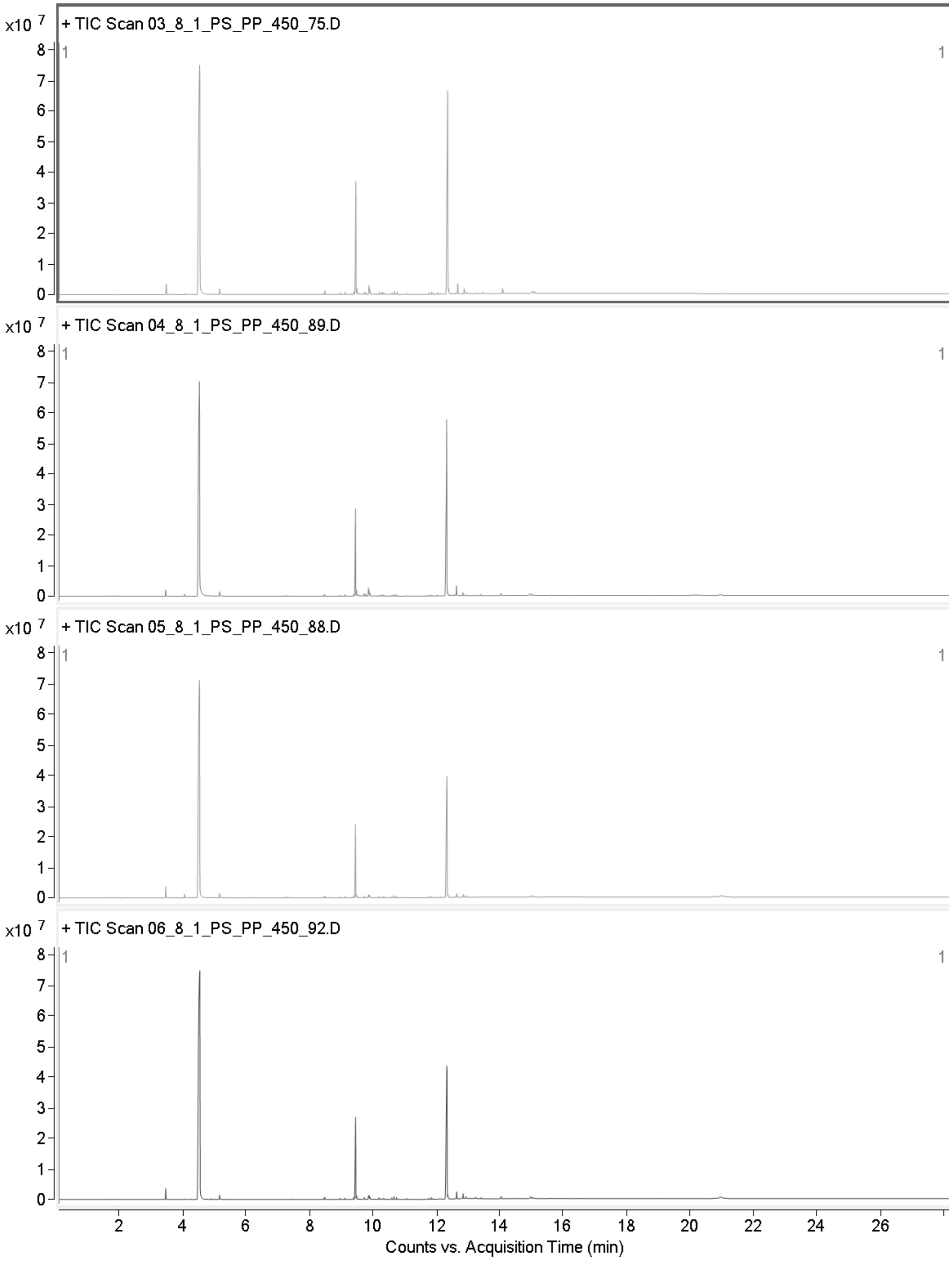


Figure A-13. Total ion current for 30 second 450°C single-shot experiments of 1:8 PP:PS.

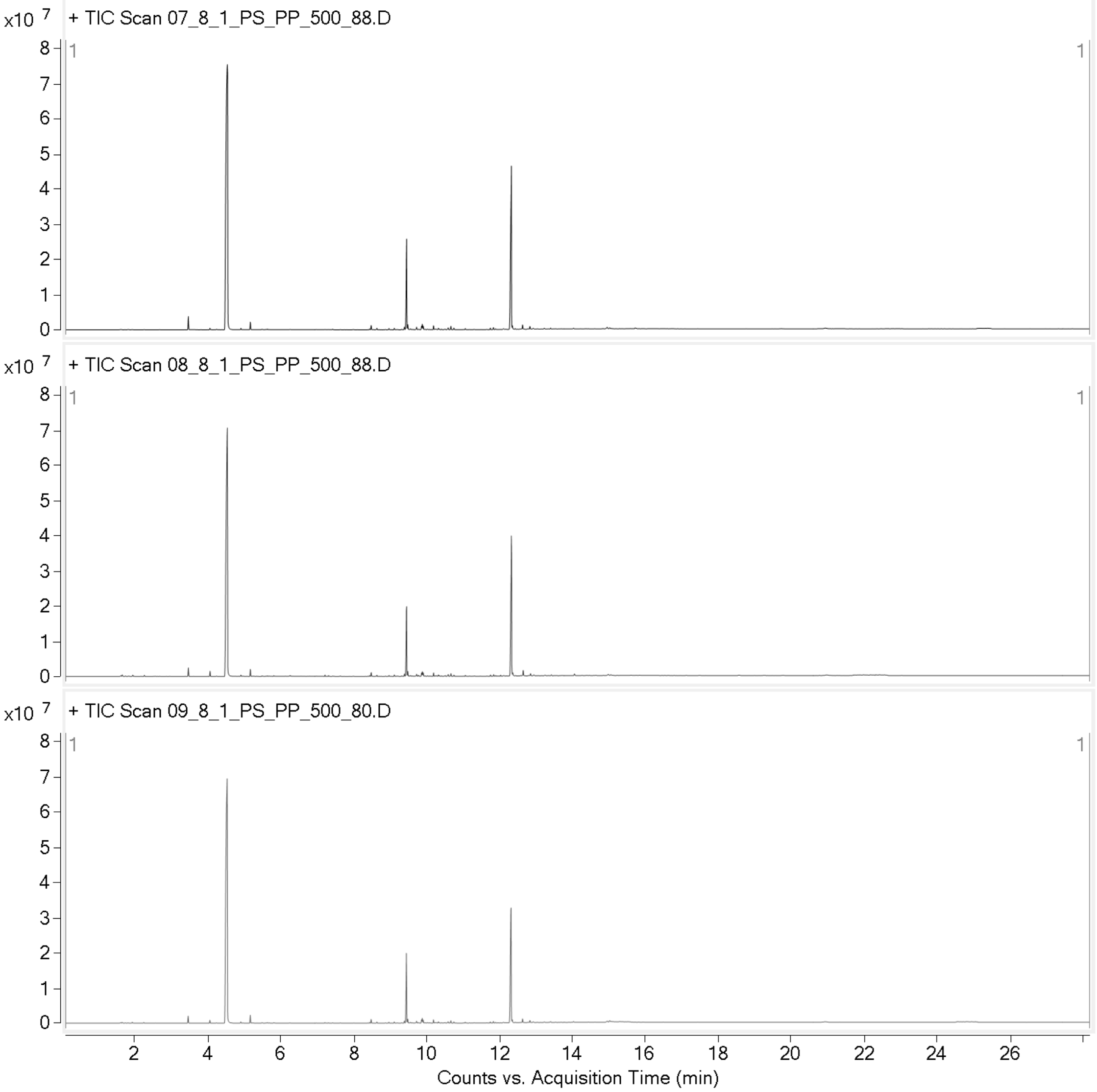


Figure A-14. Total ion current for 30 second 500°C single-shot experiments of 1:8 PP:PS.

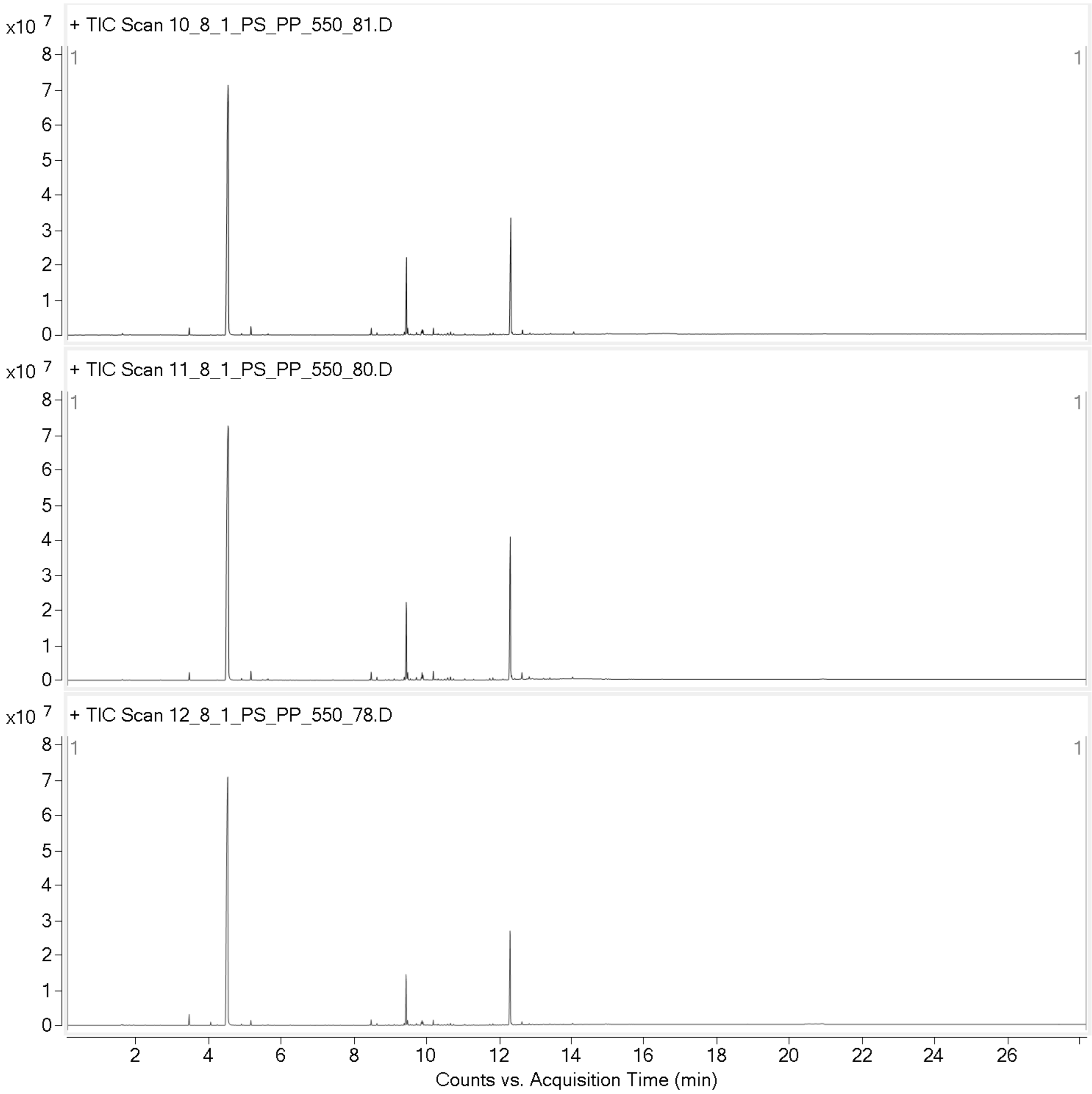


Figure A-15. Total ion current for 30 second 550°C single-shot experiments of 1:8 PP:PS.

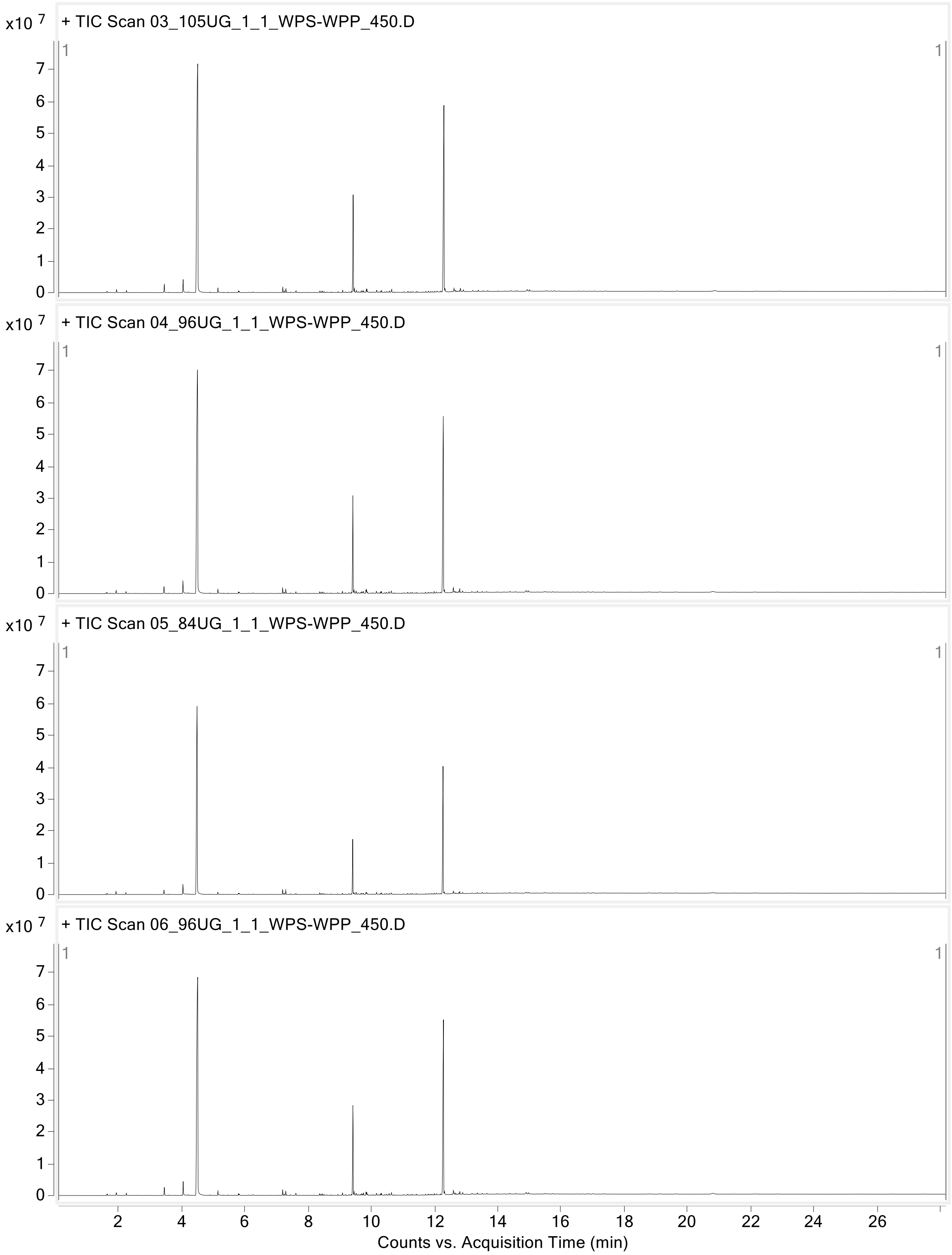


Figure A-16. Total ion current for 30 second 450°C single-shot experiments of 1:1 PP:PS.

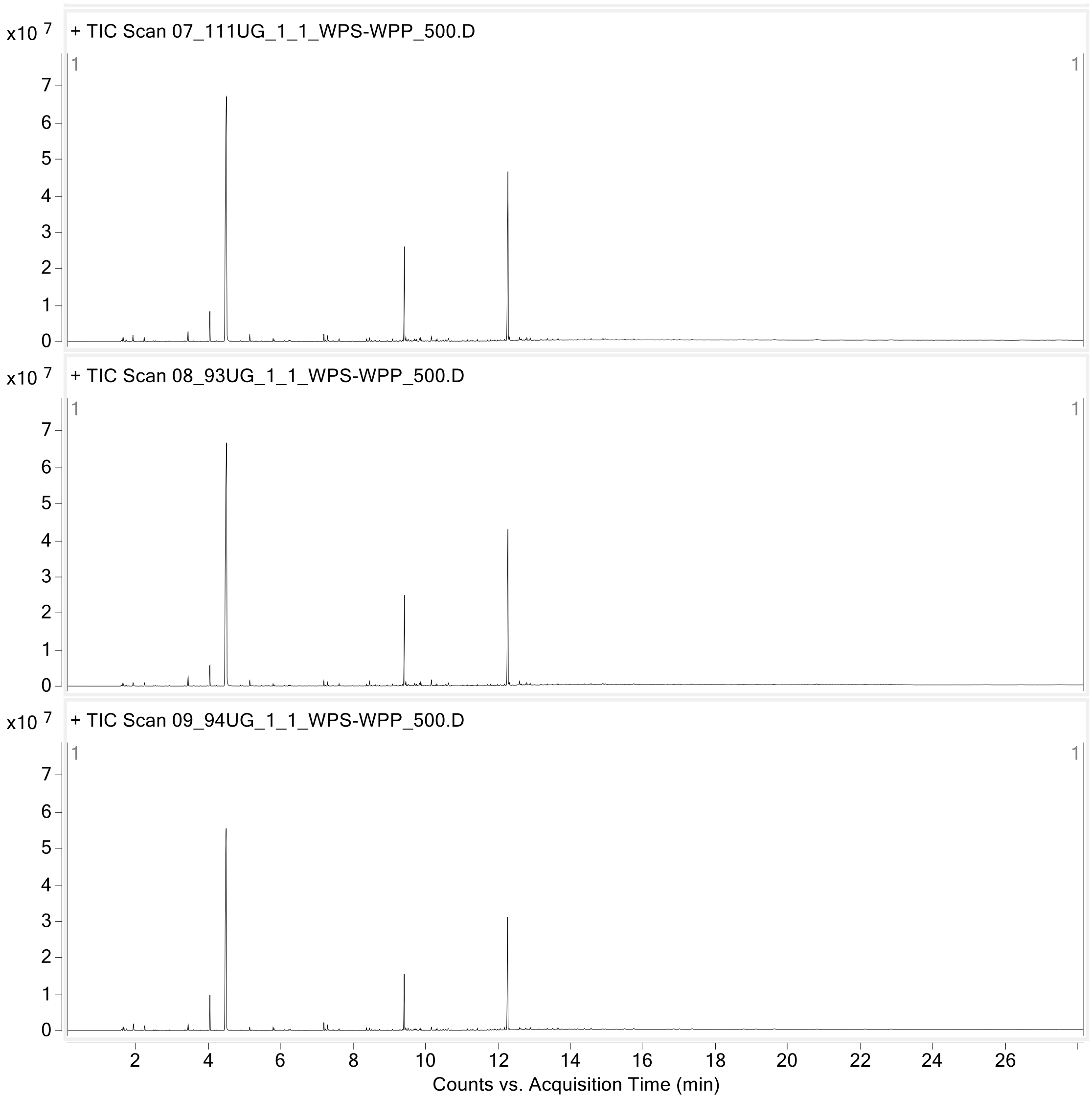


Figure A-17. Total ion current for 30 second 500°C single-shot experiments of 1:1 PP:PS.

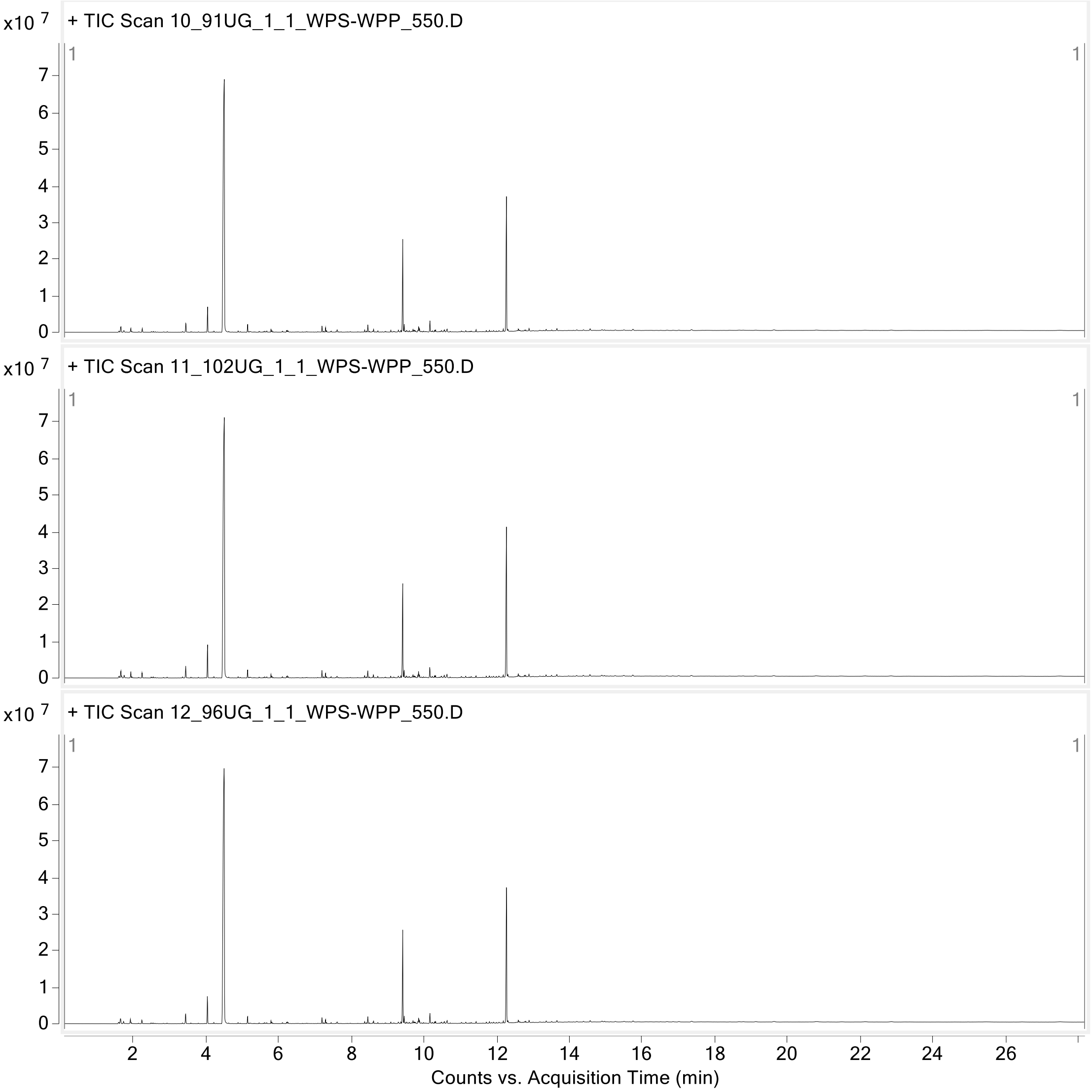


Figure A-18. Total ion current for 30 second 550°C single-shot experiments of 1:1 PP:PS.

B. Appendix B: Relative Peak Area Tabulations

B.1 Relative Area Sample Calculation

Table B-1 shows the target ion, retention time, integrated area of base peak, and relative area of pyrolytic products from 1:1 low-density polyethylene and polystyrene at 500°C for 30 seconds. The integrated area of the base peak is provided from MassHunter MS Quantitative Analysis, with the relative area to compounds from the same plastic type calculated as shown:

$$A_{rel,i} = \frac{A_{BP,i}}{\sum A_{BP}}$$

Table B-1. Tabulated Relative Areas for LDPE-PS Pyrolysis Products.

Compound	**Target Ion (*m/z*)**	**Plastic Produced From**	**Retention Time (min)**	**Integrated Area of Base Peak ($A_{BP,i}$)**	**Relative Area ($A_{Rel,i}$)**
C4	56	**LDPE**	3.033	5616	0.023
C6	56	**LDPE**	3.617	50864	0.069
C10	55	**LDPE**	6.439	40252	0.045
C11	55	**LDPE**	7.097	28702	0.036
C13	55	**LDPE**	8.284	24169	0.029
C14	55	**LDPE**	8.819	31692	0.039
C16	55	**LDPE**	9.815	23126	0.031
C19	55	**LDPE**	11.125	40002	0.050
C20	55	**LDPE**	11.524	40237	0.046
C21	55	**LDPE**	11.912	37980	0.050
C22	55	**LDPE**	12.287	37800	0.051
C24	55	**LDPE**	13.024	50014	0.060
C26	55	**LDPE**	13.768	53774	0.073
C27	55	**LDPE**	14.162	47307	0.060
C28	55	**LDPE**	14.598	45648	0.068
C31	97	**LDPE**	16.197	22843	0.035
C32	97	**LDPE**	16.892	30899	0.029
C33	57	**LDPE**	17.187	46893	0.006
C34	57	**LDPE**	17.697	47249	0.063
C35	57	**LDPE**	19.757	59783	0.073
C36	57	**LDPE**	21.079	39508	0.060
C39	57	**LDPE**	26.73	2837	0.006
Toluene	91	*PS*	4.804	2648687	0.033
Styrene	104	*PS*	5.795	41737241	0.520

Styrene Dimer	91	*PS*	10.559	16932843	0.215
Styrene Trimer	91	*PS*	13.455	20056223	0.232

B.2 Relative Areas for LDPE-PS Samples

Table B-2. Relative Areas for LDPE-PS Mixture Runs

Fraction PS	Temp	C4	C6	C10	C11	C13	C14	C16	C19
0.9	450	0.006	0.008	0.010	0.006	0.004	0.008	0.008	0.011
0.9	450	0.007	0.024	0.029	0.022	0.020	0.025	0.023	0.038
0.9	450	0.006	0.019	0.022	0.018	0.017	0.027	0.021	0.043
0.9	450	0.008	0.022	0.027	0.019	0.015	0.026	0.017	0.025
0.9	500	0.007	0.063	0.050	0.036	0.030	0.039	0.029	0.050
0.9	500	0.023	0.069	0.045	0.036	0.029	0.039	0.031	0.050
0.9	500	0.037	0.073	0.046	0.034	0.030	0.036	0.027	0.047
0.9	500	0.011	0.078	0.047	0.037	0.030	0.041	0.031	0.052
0.9	550	0.036	0.088	0.053	0.040	0.031	0.037	0.030	0.054
0.9	550	0.039	0.094	0.058	0.041	0.030	0.037	0.031	0.048
0.9	550	0.037	0.092	0.062	0.041	0.032	0.042	0.030	0.055
0.9	550	0.044	0.104	0.056	0.043	0.030	0.039	0.032	0.052
0.1	450	0.014	0.016	0.019	0.018	0.020	0.025	0.021	0.044
0.1	450	0.010	0.013	0.015	0.016	0.017	0.023	0.025	0.047
0.1	450	0.008	0.010	0.013	0.014	0.015	0.020	0.023	0.044
0.1	450	0.006	0.009	0.010	0.013	0.014	0.020	0.021	0.044
0.1	500	0.020	0.051	0.035	0.028	0.023	0.030	0.026	0.045
0.1	500	0.019	0.049	0.037	0.029	0.025	0.033	0.037	0.048
0.1	500	0.023	0.050	0.037	0.029	0.024	0.033	0.028	0.048
0.1	500	0.022	0.053	0.039	0.031	0.026	0.035	0.030	0.051
0.1	550	0.024	0.078	0.046	0.035	0.028	0.037	0.041	0.048
0.1	550	0.018	0.085	0.050	0.038	0.028	0.039	0.030	0.052
0.1	550	0.027	0.087	0.051	0.039	0.029	0.038	0.032	0.051
0.1	550	0.029	0.078	0.047	0.035	0.026	0.037	0.028	0.049
0.5	450	0.008	0.010	0.020	0.012	0.014	0.020	0.019	0.038
0.5	450	0.009	0.010	0.016	0.013	0.012	0.019	0.019	0.036
0.5	450	0.009	0.010	0.017	0.013	0.015	0.020	0.020	0.039
0.5	450	0.010	0.010	0.018	0.013	0.012	0.019	0.020	0.032
0.5	500	0.016	0.025	0.028	0.026	0.029	0.031	0.032	0.037
0.5	500	0.016	0.025	0.027	0.027	0.030	0.033	0.034	0.036
0.5	500	0.015	0.024	0.026	0.028	0.027	0.031	0.031	0.037
0.5	500	0.015	0.023	0.028	0.027	0.028	0.032	0.035	0.036
0.5	550	0.022	0.029	0.029	0.032	0.035	0.036	0.035	0.038
0.5	550	0.022	0.029	0.031	0.033	0.038	0.037	0.036	0.039
0.5	550	0.020	0.028	0.028	0.031	0.036	0.038	0.035	0.037
0.5	550	0.015	0.026	0.027	0.032	0.034	0.035	0.035	0.036

B.2 Relative Areas for LDPE-PS Samples

Table B-2 ***(continued).***Relative Areas for LDPE-PS Mixture Runs

Fraction PS	Temp	C20	C21	C22	C24	C26	C27	C28	C31	C32	C33
0.9	450	0.010	0.011	0.010	0.068	0.019	0.016	0.020	0.013	0.014	0.281
0.9	450	0.043	0.038	0.043	0.056	0.059	0.059	0.063	0.030	0.027	0.049
0.9	450	0.046	0.045	0.049	0.061	0.064	0.073	0.082	0.032	0.035	0.073
0.9	450	0.030	0.032	0.029	0.055	0.047	0.041	0.051	0.020	0.020	0.108
0.9	500	0.050	0.047	0.047	0.062	0.067	0.059	0.057	0.028	0.038	0.058
0.9	500	0.046	0.050	0.051	0.060	0.073	0.060	0.068	0.035	0.029	0.006
0.9	500	0.044	0.050	0.047	0.055	0.063	0.057	0.061	0.023	0.028	0.067
0.9	500	0.053	0.047	0.052	0.051	0.061	0.058	0.064	0.029	0.024	0.066
0.9	550	0.052	0.050	0.050	0.051	0.057	0.054	0.055	0.028	0.028	0.051
0.9	550	0.048	0.046	0.052	0.044	0.054	0.048	0.053	0.023	0.026	0.052
0.9	550	0.051	0.045	0.050	0.051	0.055	0.047	0.052	0.027	0.027	0.054
0.9	550	0.050	0.045	0.055	0.052	0.056	0.051	0.058	0.026	0.020	0.049
0.1	450	0.042	0.050	0.049	0.071	0.078	0.071	0.079	0.030	0.032	0.079
0.1	450	0.047	0.047	0.052	0.073	0.079	0.077	0.082	0.038	0.037	0.012
0.1	450	0.045	0.046	0.051	0.072	0.079	0.076	0.083	0.038	0.039	0.007
0.1	450	0.046	0.044	0.050	0.069	0.078	0.076	0.083	0.038	0.040	0.014
0.1	500	0.045	0.046	0.047	0.054	0.056	0.057	0.061	0.032	0.035	0.011
0.1	500	0.049	0.041	0.057	0.048	0.051	0.046	0.052	0.028	0.033	0.010
0.1	500	0.048	0.047	0.047	0.056	0.053	0.054	0.056	0.031	0.033	0.008
0.1	500	0.054	0.047	0.046	0.049	0.044	0.044	0.049	0.030	0.033	0.009
0.1	550	0.049	0.044	0.045	0.044	0.045	0.044	0.057	0.031	0.033	0.012
0.1	550	0.050	0.046	0.039	0.039	0.042	0.043	0.050	0.033	0.035	0.015
0.1	550	0.052	0.045	0.035	0.038	0.042	0.043	0.050	0.034	0.033	0.009
0.1	550	0.049	0.046	0.045	0.045	0.045	0.044	0.052	0.032	0.034	0.010
0.5	450	0.037	0.041	0.043	0.062	0.067	0.064	0.073	0.035	0.038	0.084
0.5	450	0.038	0.039	0.041	0.063	0.072	0.066	0.078	0.035	0.038	0.086
0.5	450	0.041	0.040	0.042	0.063	0.068	0.064	0.077	0.036	0.037	0.084
0.5	450	0.040	0.039	0.043	0.066	0.069	0.065	0.078	0.036	0.038	0.092
0.5	500	0.043	0.044	0.040	0.045	0.050	0.050	0.046	0.051	0.051	0.064
0.5	500	0.041	0.045	0.039	0.048	0.047	0.050	0.051	0.055	0.053	0.056
0.5	500	0.042	0.046	0.039	0.044	0.048	0.048	0.047	0.057	0.055	0.064
0.5	500	0.041	0.046	0.037	0.043	0.051	0.049	0.046	0.055	0.051	0.056
0.5	550	0.040	0.042	0.047	0.044	0.047	0.049	0.050	0.055	0.055	0.053
0.5	550	0.040	0.041	0.047	0.045	0.046	0.047	0.048	0.053	0.054	0.058
0.5	550	0.042	0.039	0.047	0.050	0.046	0.047	0.052	0.051	0.052	0.060
0.5	550	0.040	0.041	0.043	0.045	0.047	0.048	0.048	0.053	0.054	0.060

B.2 Relative Areas for LDPE-PS Samples

Table B-2 ***(continued).***Relative Areas for LDPE-PS Mixture Runs

Fraction PS	**Temp**	**C34**	**C35**	**C36**	**C39**	**Toluene**	**Styrene**	**Styrene Dimer**	**Styrene Trimer**
0.9	450	0.159	0.242	0.007	0.069	0.021	0.506	0.202	0.271
0.9	450	0.062	0.034	0.039	0.211	0.025	0.504	0.199	0.272
0.9	450	0.070	0.070	0.056	0.073	0.024	0.517	0.196	0.263
0.9	450	0.092	0.165	0.028	0.123	0.024	0.505	0.201	0.270
0.9	500	0.059	0.074	0.049	0.004	0.033	0.513	0.208	0.246
0.9	500	0.063	0.073	0.060	0.006	0.033	0.520	0.215	0.232
0.9	500	0.055	0.071	0.041	0.007	0.029	0.524	0.209	0.239
0.9	500	0.050	0.057	0.044	0.016	0.033	0.517	0.205	0.244
0.9	550	0.050	0.046	0.042	0.016	0.041	0.551	0.217	0.191
0.9	550	0.046	0.060	0.044	0.027	0.035	0.563	0.212	0.190
0.9	550	0.047	0.056	0.039	0.007	0.035	0.544	0.215	0.207
0.9	550	0.047	0.047	0.037	0.004	0.039	0.556	0.208	0.198
0.1	450	0.073	0.070	0.066	0.034	0.017	0.534	0.194	0.255
0.1	450	0.085	0.087	0.077	0.042	0.022	0.618	0.193	0.168
0.1	450	0.086	0.091	0.081	0.059	0.014	0.668	0.166	0.152
0.1	450	0.087	0.095	0.083	0.061	0.017	0.731	0.130	0.123
0.1	500	0.069	0.089	0.075	0.065	0.026	0.693	0.168	0.113
0.1	500	0.068	0.101	0.077	0.062	0.023	0.632	0.196	0.149
0.1	500	0.067	0.099	0.077	0.051	0.020	0.777	0.118	0.085
0.1	500	0.067	0.109	0.078	0.056	0.017	0.773	0.125	0.086
0.1	550	0.060	0.083	0.064	0.051	0.016	0.797	0.108	0.079
0.1	550	0.062	0.081	0.070	0.054	0.020	0.804	0.115	0.061
0.1	550	0.056	0.087	0.068	0.054	0.034	0.806	0.107	0.053
0.1	550	0.056	0.099	0.061	0.052	0.023	0.720	0.154	0.103
0.5	450	0.081	0.080	0.087	0.067	0.019	0.590	0.192	0.199
0.5	450	0.081	0.081	0.090	0.060	0.013	0.512	0.205	0.270
0.5	450	0.077	0.083	0.093	0.056	0.019	0.514	0.208	0.259
0.5	450	0.080	0.078	0.083	0.058	0.020	0.544	0.203	0.232
0.5	500	0.076	0.065	0.076	0.073	0.015	0.603	0.221	0.161
0.5	500	0.072	0.068	0.074	0.074	0.015	0.542	0.238	0.204
0.5	500	0.078	0.066	0.073	0.075	0.013	0.561	0.230	0.196
0.5	500	0.078	0.069	0.077	0.076	0.013	0.623	0.210	0.154

Fraction PS	Temp	C34	C35	C36	C39	Toluene	Styrene	Styrene Dimer	Styrene Trimer
0.5	550	0.064	0.063	0.064	0.071	0.018	0.754	0.148	0.079
0.5	550	0.066	0.061	0.066	0.067	0.019	0.697	0.197	0.087
0.5	550	0.066	0.063	0.067	0.065	0.016	0.684	0.196	0.103
0.5	550	0.069	0.069	0.070	0.071	0.015	0.649	0.223	0.112

B.3 Relative Areas for PP-PS Runs

Table B-3. Relative Areas for PP-PS Mixture Runs

Fraction PS	Temp.	C3	C5	C9	C12	C15	C18	C22	Styrene	Dimer	Trimer
0.9	450	0.103	0.181	0.488	0.039	0.117	0.030	0.041	0.496	0.168	0.335
0.9	450	0.100	0.174	0.545	0.006	0.105	0.030	0.039	0.483	0.172	0.346
0.9	450	0.085	0.162	0.554	0.029	0.108	0.028	0.035	0.516	0.157	0.326
0.9	450	0.092	0.176	0.485	0.024	0.142	0.038	0.042	0.531	0.145	0.323
0.9	500	0.204	0.108	0.536	0.034	0.084	0.020	0.014	0.571	0.132	0.297
0.9	500	0.253	0.195	0.402	0.040	0.073	0.019	0.018	0.576	0.122	0.302
0.9	500	0.279	0.199	0.382	0.040	0.066	0.015	0.019	0.593	0.115	0.293
0.9	550	0.365	0.151	0.352	0.032	0.064	0.017	0.019	0.596	0.129	0.274
0.9	550	0.246	0.121	0.530	0.019	0.049	0.014	0.021	0.647	0.094	0.259
0.5	450	0.081	0.157	0.515	0.036	0.129	0.034	0.047	0.534	0.149	0.317
0.5	450	0.083	0.171	0.472	0.039	0.142	0.041	0.051	0.501	0.156	0.342
0.5	450	0.084	0.161	0.475	0.043	0.145	0.042	0.050	0.534	0.123	0.343
0.5	450	0.087	0.172	0.497	0.037	0.129	0.036	0.042	0.502	0.162	0.336
0.5	500	0.169	0.161	0.510	0.019	0.090	0.027	0.024	0.550	0.137	0.313
0.5	500	0.183	0.150	0.526	0.017	0.076	0.024	0.024	0.551	0.144	0.305
0.5	500	0.108	0.173	0.559	0.021	0.089	0.026	0.024	0.600	0.112	0.287
0.5	550	0.250	0.119	0.479	0.018	0.087	0.027	0.019	0.592	0.148	0.260
0.5	550	0.246	0.127	0.499	0.015	0.074	0.023	0.016	0.575	0.151	0.274
0.5	550	0.237	0.129	0.503	0.015	0.077	0.022	0.016	0.587	0.141	0.272
0.1	450	0.092	0.185	0.451	0.036	0.145	0.038	0.054	0.549	0.086	0.365
0.1	450	0.105	0.189	0.476	0.037	0.138	0.007	0.048	0.600	0.072	0.328
0.1	450	0.083	0.161	0.485	0.044	0.148	0.034	0.045	0.572	0.070	0.358
0.1	450	0.075	0.155	0.438	0.040	0.181	0.039	0.072	0.631	0.080	0.289
0.1	500	0.207	0.160	0.496	0.017	0.079	0.022	0.018	0.672	0.067	0.261
0.1	500	0.195	0.171	0.494	0.017	0.080	0.023	0.020	0.633	0.086	0.280
0.1	500	0.190	0.184	0.505	0.020	0.067	0.018	0.015	0.740	0.045	0.215
0.1	500	0.201	0.153	0.484	0.017	0.098	0.030	0.016	0.717	0.042	0.241
0.1	550	0.289	0.131	0.470	0.013	0.066	0.019	0.013	0.763	0.056	0.181

0.1	550	0.264	0.134	0.488	0.014	0.067	0.019	0.014	0.726	0.067	0.207
0.1	550	0.250	0.129	0.491	0.013	0.068	0.025	0.023	0.745	0.060	0.195
0.1	550	0.244	0.137	0.486	0.015	0.083	0.019	0.017	0.803	0.038	0.159

C. Appendix C: Experimental Equipment Details

C.1 Frontier Pyrolyzer System

Figure C-1 shows the schematic of the Frontier 3030D Pyrolyzer with auto-sampler as attached to the gas chromatograph (GC) inlet. The following are numbered: (1) Helium Carrier Gas from GC Electronic Flow Controller, (2) Cooling Air, (3) Nitrogen Furnace Purge, (4) Helium for Auto-Shot Recovery, (5) Helium Carrier to Inlet (diverted to 1), (6) Air Outlet, (7) Cup Recovery Relief, (8) Nitrogen Purge Flow, (9) Septum Purge, and (10) Split Purge.

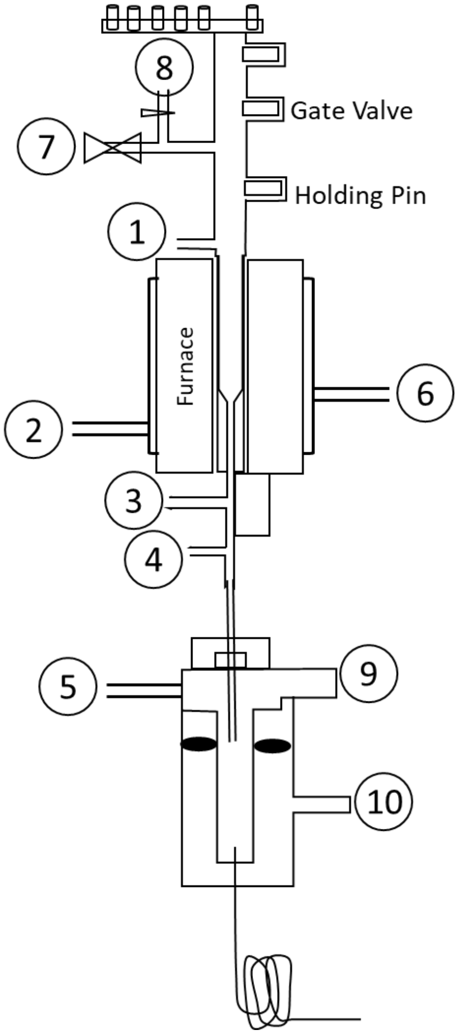
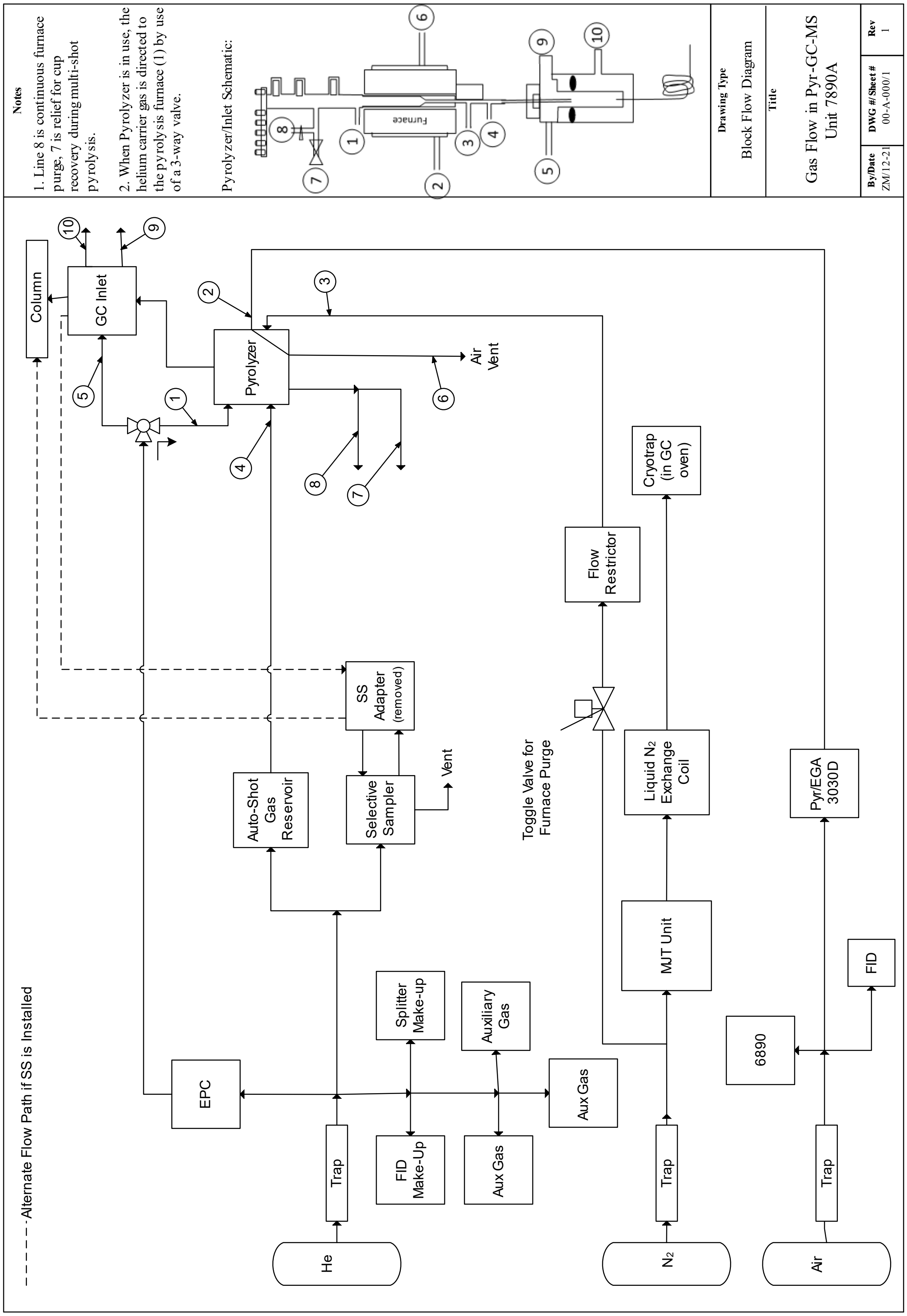


Figure C-1. Frontier Pyrolyzer Schematic



- - - - - Alternate Flow Path if SS is Installed

Notes

1. Line 8 is continuous furnace purge, 7 is relief for cup recovery during multi-shot pyrolysis.

2. When Pyrolyzer is in use, the helium carrier gas is directed to the pyrolysis furnace (1) by use of a 3-way valve.

Pyrolyzer/Inlet Schematic:

Drawing Type	Block Flow Diagram
Title	Gas Flow in Pyr-GC-MS Unit 7890A
By/Date	ZM/12-21
DWG #/Sheet #	00-A-000/1
Rev	1

Figure C-2. 7890A Pyrolysis-GC-MS System Gas Flows

C.2 Single-Shot Experiment Operation Principle

1. Sample cup shutter, gate valve, and holding pin open, then sample cup from previous run is ejected from pyrolysis furnace via 3 pulses of helium (Auto-Shot Recovery) – shown as 4 in **Figure C-1.**
2. Sample cup shutter, gate valve, and holding pin close.
3. Desired sample cup is rotated to above furnace in top auto-shot carousel.
4. Sample cup is introduced to pyrolyzer system upon opening of sample cup shutter and gate valve, landing on holding pin.
5. Pyrolyzer reaches set temperature and cryo-trap reaches set temperature.
6. Holding pin is dropped, sample pyrolysis time starts.
7. After pyrolysis time, cryo-trap turns off and GC-MS analysis begins.
8. After full GC sequence is complete, back to Step 1.

C.3 Single-Shot Experiment Pyrolyzer Control Parameters

A single-shot method at the set temperature for 0.5 minutes was used, with the MJT (Microject Cryo-Trap) activated. It was found that using this method does not actually limit pyrolysis to the 0.5 minutes set, as the sample cup remains in the furnace throughout the GC method. In order to collect data for the set time, the Selective Sampler must be installed.