

CHAPTER IV
ANALYSIS OF A TIRE-DERIVED OIL USING GC × GC / TOF-MS FOR
BETTER IDENTIFICATION AND GROUPING OF HYDROCARBON
COMPOUNDS

4.1 Abstract

A tire-derived oil (TDO) consists of many types of hydrocarbons such as mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs) and polar-aromatics (PPAHs). Previously, a GC/MS has been used to analyze the components in TDOs, and 38 hydrocarbon species were found and identified. However, the drawback of a regular GC/MS is that it cannot separate the hydrocarbon species with the same retention time because boiling points, vapor pressures and mass spectral fragmentation patterns are indistinguishable. Therefore, hundreds of hydrocarbons in the oil could not be observed and identified due to the overlapped mass spectra. At present, no work has been reported on analysis of a tire-derived oil using Two-Dimensional Gas Chromatography coupled with a Time-of-Flight Mass Spectrometry (GC × GC / TOF-MS) for hydrocarbon species. The objective of this work was to examine the components in a tire-derived oil, and completely report the results in terms of 2D (contour plot) and 3D (surface plot) plots of total ion chromatograms for outstanding groups of hydrocarbon species such as saturated hydrocarbons (SATs), olefins (OLEs), terpenes (TERs), MAHs, DAHs, PAHs, and PPAHs, including sulfur compounds. Maltenes (liquid fractions without asphaltene) were collected and analyzed by using a SIMDIST GC, and GC × GC / TOF-MS. As a result, the SATs consists of aliphatic hydrocarbons starting at C13, C14 to C16. The OLEs consists of di-olefins and tri-olefins. The TERs consists of Carene and Limonene. The MAHs is categorized into two groups; that are, (a) mono-aromatics with saturated substituents (MAHs-SS) such as indanes, alkylbenzenes, and tetralins, and (b) mono-aromatics with unsaturated substituents (MAHs-US) such as indenenes and alkenylbenzene. The DAHs consists of naphthalene and alkyl-naphthalenes. The PAHs consists of phenanthrene, anthracene, fluorene, and pyrene. Finally, the PPAHs consists of thiophenes, benzothiohenes, and dibenzothiophenes.

Keywords: GC × GC TOF/MS, tire-derived oil, pyrolysis, hydrocarbon species, grouping, waste tire

4.2 Introduction

Due to the growth of population and development of transportation in the world, a large number of cars have been increased rapidly resulting in a lot of tires consumed in every year (ETRMA, 2011). Waste tires become more serious environmental problem because of non-biodegradable properties. Therefore, waste tire management needs to be implemented. Pyrolysis has been introduced in this decade as a renewable waste tire recycling technology. The products are liquid (e.g., oil), gas (e.g., methane, ethane, ethylene, propane, propylene, H₂, H₂S, CO, and CO₂), and solid (e.g., char or carbon black). Tire-derived oil (TDO) is a dark brown/black colored, medium viscosity oil with sulphur or aromatic odor. This liquid is very complex, containing more than 100 compounds in majority (Cunliffe *et al.*, 1998). Among those, they were saturated hydrocarbons, olefins, and aromatics, for examples. Dai *et al.* used SiO₂/Al₂O₃ liquid column chromatography to separate a TDO, and analyzed by using GC/MS. They reported that the hydrocarbon species in TDOs was 26.77 wt.% alkanes, 42.09 wt.% aromatics, 26.64 wt.% non-hydrocarbon, and 4.05 wt% asphaltene, and found that the aromatics were the mixture of mono-aromatics, di-aromatics, and poly-aromatics (Dai *et al.*, 2001). William and Bottrill used SiO₂/Al₂O₃ liquid column chromatography to separate sulfur-polycyclic aromatic hydrocarbons, and then analyzed by using a normal GC/MS. They found that these compounds were 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 2,5-dimethylthiophene, 2,4-dimethylthiophene, 2,3-dimethylthiophene, 3-ethylthiophene, 2-isopropylthiophene, 2-tert-butylthiophene and their derivatives (Williams *et al.*, 1995). Pakdel *et al.* studied the production of *dl*-limonene by vacuum pyrolysis of used tire using a normal GC/MS, and found that *dl*-limonene was mixed in alkane, alkene, and poly-aromatics fractions. However, the peaks were not easy to be resolved because they came out nearly at the same retention time and had similar boiling point (Pakdel *et al.*, 2001). Moreover,

Lagesgoiti *et al.* characterized the liquid product in TDO by using a normal GC/MS. They found that the chromatograms of poly-aromatics and polar-aromatics were not explicitly separated from one another, and it was difficult to interpret the results (Laresgoiti *et al.*, 2004). Boxiong *et al.* revealed hydrocarbon species in TDOs by using a normal GC/MS to investigate the influence of zeolite USY catalyst, and found 38 hydrocarbon species of aromatic hydrocarbons in the light fraction that are the mixtures of saturated hydrocarbons (with aliphatic and branch chain), olefins, naphthenes, and aromatics. They also found that the chromatograms showed some of saturated hydrocarbons and olefins that could not be identified because they evolved at the same retention time (Boxiong *et al.*, 2007). From the literature reviews, several authors used a normal GC/MS, and reported that the chromatograms overlapped and might not bring about accuracy data analysis. In conclusion, it is not easy to resolve overlapped peaks from chromatograms of TDOs using a normal GC/MS; therefore, the separation of a complex mixture of TDOs requires highly-advanced technology with high chromatogram resolution.

Comprehensive 2D gas chromatography with time-of-flight mass spectrometry (GC \times GC- TOF/MS) is a new technique that has high performance to resolve the complexity of compounds. GC \times GC - TOF/MS consisted of two consecutively-connected columns and TOF/MS as a detector. The key to the GC application of comprehensive chromatography analysis was the ability to rapidly pulse segments of effluent from Column 1 to Column 2. The first column (a primary non-polarity column) can separate the components based on carbon number, and it consequently provides the second column (a secondary polar column) with a series of sub-samples containing the same carbon number that can be further separated based on the polarity. The second column does not need to create a large peak capacity because the component from the first column is limited (Phillips *et al.*, 1999). Time-of-flight (TOF/MS) instrument is able to scan at the high scan rates of ≥ 50 spectra/second. The data can be collected at high rates, which are shown obviously at separated retention time and accurate quantification (Dallüge *et al.*, 2002). After that, the raw data are plotted into two-dimension chromatogram (contour plot) and three-dimension chromatogram (surface plot). In conclusion, this technique can give high resolution of chromatogram and better results than a normal

GC/MS. Indeed, GC \times GC - TOF/MS is equipped with a software that can deconvolute chromatograms for identification as well as accurate quantification (Marriott *et al.*, 2002). The analysis of an unresolved complex mixture such as oil spill, rich biodegraded crude oil, cigarette smoke, and standard polycyclic aromatics have been well accomplished by using this technique (Dallüge *et al.*, 2002, Nelson *et al.*, 2006, Melbye *et al.*, 2009, Manzano *et al.*, 2012). To our knowledge, no work has been done to analyze TDO by using GC \times GC - TOF/MS. The purposes of this study were to reveal hydrocarbon species in TDOs using GC \times GC - TOF/MS, and the LECO ChromaTOF® software was used to classify the obtained data into different groups of hydrocarbons, including sulphur compounds. The hydrocarbon groupings are presented in contour plots, and some abundantly-observed compounds in each group are also identified and reported.

4.3 Experimental

4.3.1 Pyrolysis of Waste Tire

Figure 4.1 displays the experimental diagram. A used passenger tire tread, Bridgestone TURANZA GR-80, was shredded and sieved to a size range of 8-18 mesh. The tire sample was pyrolyzed in the reactor where the temperature was ramped from room temperature to the final temperature of 500°C with the ramping rate of 10 °C min⁻¹, and kept at the final temperature for one hour to ensure the total conversion of tire. A 25 ml min⁻¹ nitrogen was used to purge the reactor before the experiment and to carry the product out of the reactor. The obtained product was passed through the ice-salt condensing system containing two consecutive containers in order to separate the liquid product from incondensable compounds. After the experiment, the solid and liquid were weighed to determine the product distribution. The amount of gas was calculated from mass balance. Only the oil was brought to analysis in this study. It was first dissolved in n-pentane with the ratio of 40:1 (n-pentane:oil) to separate asphaltene. The clear solution after filtration is called maltene.

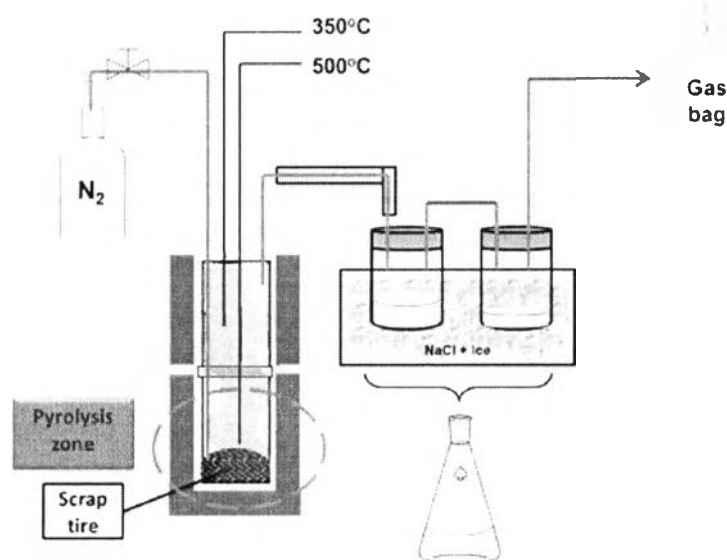


Figure 4.1 Schematic of pyrolysis experiment.

4.3.2 Analysis Using GC × GC – TOF/MS

The GC × GC–TOF/MS system was composed of an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a thermal modulator, and a Pegasus® 4D TOF-MS (LECO, St. Joseph, MI, USA). The GC was installed with two columns: the first column was a non-polar Rtx 5 silms® (30m x 0.25 mm i.d. x 0.25 μm film thickness), and the second column a Rxi®-17 ms (1.10 m x 0.10 mm i.d. x 0.10 μm film thickness). Both columns were made by Thames Restek (Sounderton, UK). The main GC oven was operated from at 50 °C with 2 minute holding at the beginning and then ramped to 310 °C at 5 °C min⁻¹ with 10 minute holding at 310 °C, and the secondary oven was operated at 60 °C held for 2 minutes at the beginning and ramped to 320 °C at 5 °C min⁻¹ with 10 minute holding at the final temperature. One μl of the 10 mg/ml maltenes in carbondisulfide (CS₂) was injected via a splitless injector at 250 °C using He as the carrier and a constant column flow rate of 1.0 ml/min. The modulator was operated under modulation timing of 4-s cycle time and 0.5-s holding time in the release position. The nitrogen cryogen coolant maintained the temperature of the modulation trap to at least 30 °C. A Pegasus 4D® TOF/MS instrument was used to acquire mass spectral data, using -70 V electron impact ionization. The ion source temperature was set at 250 °C. The

detector voltage was set at 1600 V. The transfer line temperature was 250 °C. The mass range collected was from 35 to 500 m/z , with 100 spectra/s transferred to the data station. The data processing was set S/N value of 10, match required to combine 500, and dt that was used to calculate the percentage area. Data were recorded and analyzed using the LECO ChromaTOF® software. The NIST library provided with the instrument was used for spectral searching. The analysis was repeated for 3 times.

4.4 Results and Discussion

4.4.1 Components in Tire-derived Oils from GC × GC TOF/MS

One of the advantages of GC × GC – TOF/MS is the power to separate a complex mixture of components, like a tire-derived oil. The two columns were installed; the first column (a primary non-polarity column) can separate the components based on carbon number, and the second column (a secondary polar column) can separate the chemicals that have the same carbon number based on the polarity. Figure 4.2(a) shows the contour plot of total ion chromatogram (2D TIC) of the maltene. It indicates that the conditions used to analyze the tire-derived oil are satisfied to separate the complex components, which were found in a total of more than 1,500 compounds. As the structural complexity of the components increases, partial overlap between component classes can occur even though they are shown by GC × GC-TOF/MS in the total ion chromatogram. However, the GC × GC – TOF/MS can reveal the separation of components in the overlap chromatograms as seen on the surface plot of total ion chromatogram (3D plot) in Figure 4.2(b) because the secondary column (the polar column) can separate the components with different polarities, which emerge at the same retention. These components are separated layer by layer as seen in the profile on the contour plot, continuing as the carbon number increases. Subsequently, all hydrocarbon compounds were identified using the NIST database.

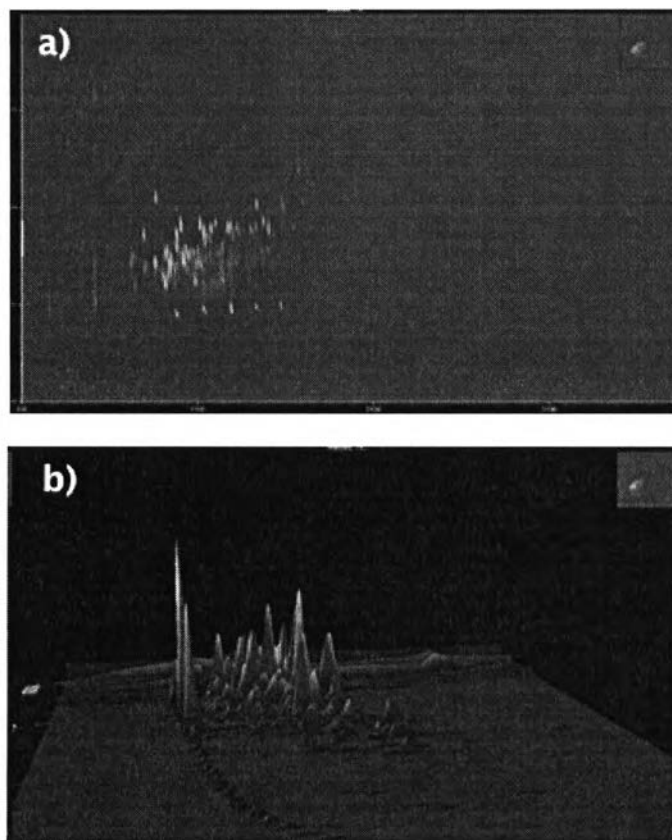
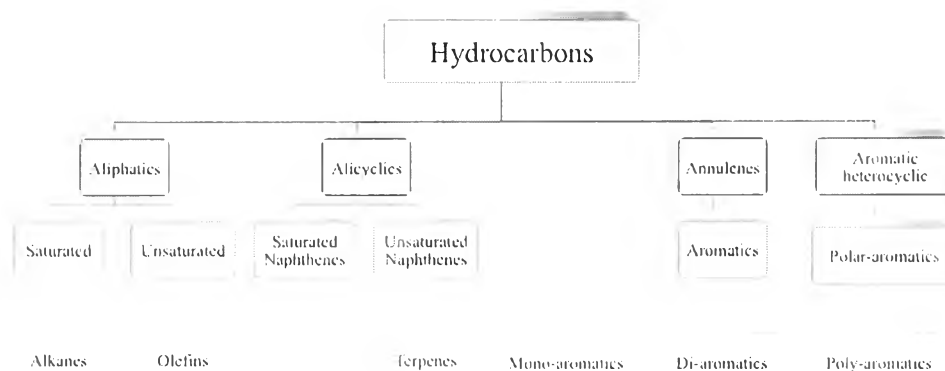


Figure 4.2 Total ion chromatogram of the maltene :(a) contour plot and (b) surface plot.

4.4.2 Grouping of Hydrocarbons in TDO Using Automate LECO ChromaTOF® Software

According to the IUPAC, hydrocarbon species are of different types, depending upon the types of carbon-carbon bonds present in the molecules; therefore, they can be classified into three main categories – (i) aliphatic hydrocarbons, (ii) alicyclic hydrocarbons or naphthene, and (iii) aromatic hydrocarbons are shown in Scheme 4.1. Aliphatic hydrocarbons classified into two classes: (i) paraffins or saturated hydrocarbons, and (ii) olefins or unsaturated hydrocarbons. Naphthene or alicyclic hydrocarbons are classified into two classes: (i) saturated alicyclic hydrocarbons, and (ii) unsaturated alicyclic hydrocarbons or terpenes. Annulenes are hydrocarbons with alternating single and double bonds, like Benzene which is a six-membered annulene. The aromatic hydrocarbons are classified into four classes: (i) mono-aromatic hydrocarbons (MAHs), (ii) di-

aromatic hydrocarbons (DAHs), (iii) poly-aromatic hydrocarbons (PAHs), and (iv) aromatic heterocyclic compounds or so-called polar-aromatic hydrocarbons (PPAHs) (IUPAC, 1997a; IUPAC, 1997b; IUPAC, 1997c; IUPAC, 1997d; IUPAC, 1997e; IUPAC, 1997f; IUPAC, 1997g).

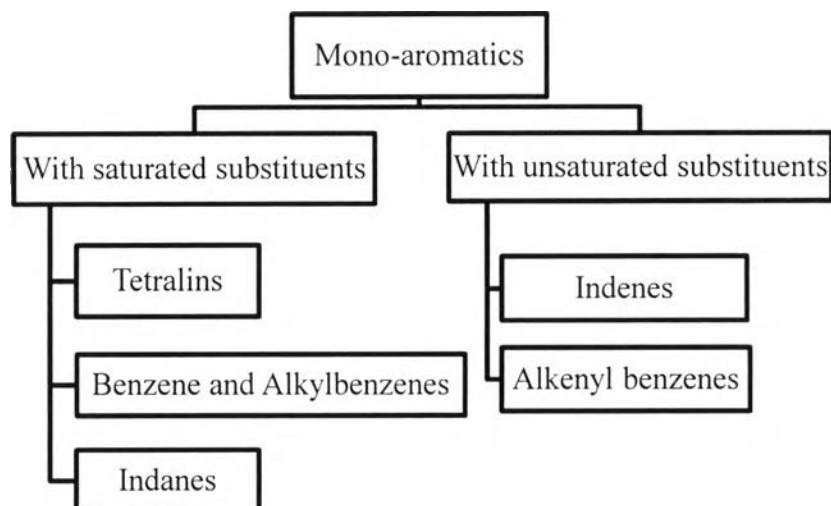


Scheme 4.1 Classification of hydrocarbons in TDO.

The ChromaTOF® software was used to process the raw data to peak table, and succeeded in classification within 180 min. Based on IUPAC, the components are thus categorized into groups according to their chemical structures; namely, mono-aromatics (MAHs), saturated hydrocarbons (SATs), olefins (OLEs), terpenes (TERs), di-aromatics (DAHs), poly-aromatics (PAHs), and polar-aromatics (PPAHs). However, due to high capability of the GC x GC-TOF/MS, better classification of each group can be done in details as follows.

4.4.2.1 *Mono-aromatics (MAHs)*

MAHs are the most valuable group of chemicals in the petrochemical industry. Some of them play an important role as upstream petrochemicals in either polymer or advanced material industries. Two main classes of MAHs are mono-aromatics with saturated substituents (MAHs-SS) and mono-aromatics with unsaturated substituents (MAHs-US) as illustrated in Scheme 4.2.



Scheme 4.2 Classification of mono-aromatic group.

Scheme 4.2 describes the classification of mono-aromatics into those with saturated substituents composed of three species that are benzene, alkylbenzenes, indanes, and tetralins, and those with unsaturated substituents of two groups that are indenes and alkenylbenzenes (IUPAC, IUPAC). Some species abundantly found in each class of MAHs and other groups are shown in Table 4.1. Moreover, the total ion chromatogram of MAHs, which indicates the region of each class based on carbon number, are depicted in Figure 4.3 for easy identification and view. The peak markers (dots) in Figure 4.3 locate the classes of MAHs found in the tire-derived oil. The carbon numbers of MAHs include C9, C10, C11, C12, C13, and C14, starting from left to right, accordingly. The C9 – C14 MAHs present in majority are depicted in Table 4.2, for examples.

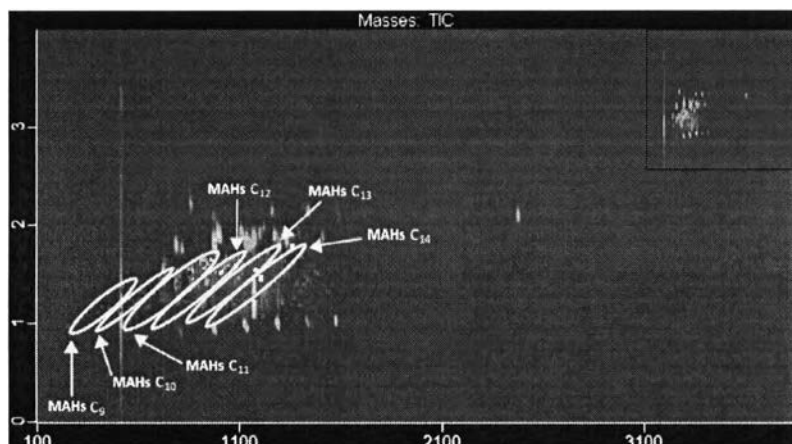



















Figure 4.3 Total ion chromatogram with peak markers of MAHs classified based on carbon number.

Table 4.2 Examples of MAHs found in each carbon number

Carbon number	Hydrocarbon species of MAHs		
9	 1-ethyl-2-methylbenzene	 2,3-dihydro-1H-indene	 1,2,3-trimethylbenzene
10	 1-methyl-2-propylbenzene	 4-methyl-2,3-dihydro-1H-indene	 butylbenzene
11	 cyclopentylbenzene	 1,6-dimethyl-2,3-dihydro-1H-indene	 6-methyl-1,2,3,4-tetrahydronaphthalene
12	 (<i>E</i>)-hex-4-en-1-ylbenzene	 1,1,5-trimethyl-2,3-dihydro-1H-indene	 pent-4-en-1-ylbenzene
13	 1,1-dimethyl-3-vinyl-2,3-dihydro-1H-indene	 (<i>E</i>)-2-(buta-1,3-dien-1-yl)-1,3,5-trimethylbenzene	 1-methyl-3-propyl-1H-indene
14	 1,2-di(isobut-3-en-2-yl)benzene	 3-ethyl-1-isopropyl-1H-indene	

4.4.2.2 Saturated Hydrocarbons (SATs)

Since SATs are defined as the hydrocarbons with only single bonds of C-C according to the chemical structure (IUPAC). As a result, the compounds in SATs in the TDO are not classified into classes, but rather done based on carbon number. The SATs are found to consist of aliphatic hydrocarbons starting at C13, C14, and C16 as depicted in Figure 4.4, which shows the classes of SATs found in TDO with peak markers based on carbon number: C13, C14, and C16 from left to right. The examples of hydrocarbons in each carbon number are shown in Table 4.3.

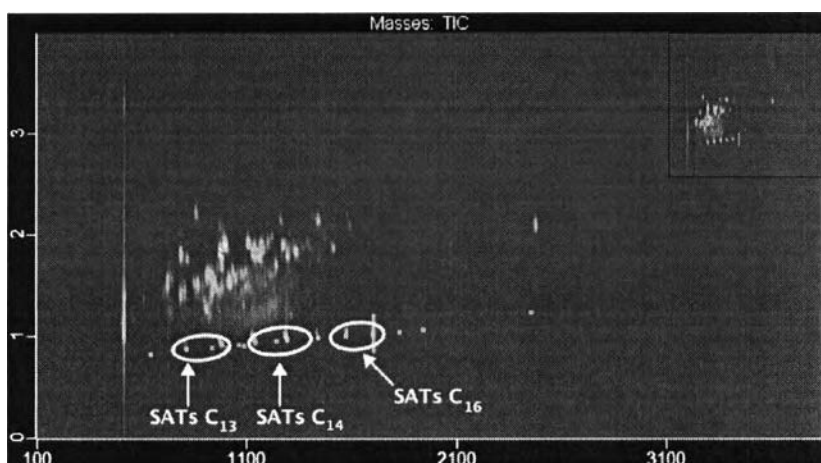


Figure 4.4 Total ion chromatogram with peak markers of SATs classified based on carbon number.

Table 4.3 Examples of SATs found in each carbon number

Carbon number	Hydrocarbon species of SATs		
13	 tridecane	 2,6,8-trimethyldecane	 5,7-dimethylundecane
14	 tetradecane	 2,3-dimethyldodecane	 3,8-dimethylundecane
16	 hexadecane		

4.4.2.3 Olefins (OLEs)

The OLEs are hydrocarbons with the carbon-carbon bond and carbon-hydrogen, which has at least one double bond of carbon-carbon present in the chemical structure (IUPAC). As a result, OLEs in the TDO can be classified into two classes: those with straight chain, and those with branching as shown in Table 4.1. However, based on carbon number, they consist of unsaturated hydrocarbons, also starting at C8, C9, C10, C11, C12 and C13 as grouped in Figure 4.5 from left to right. The examples of hydrocarbons in each carbon number are shown in Table 4.4.

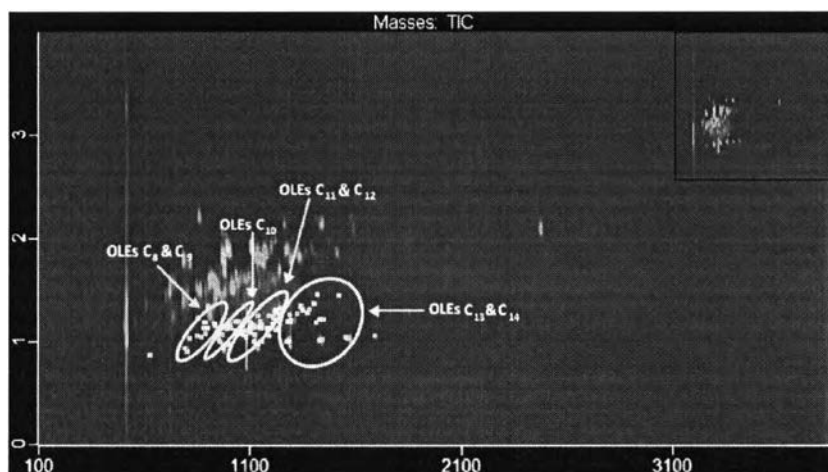
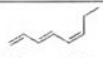
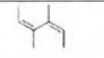
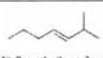

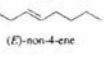
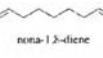
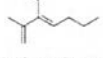
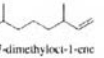
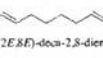
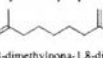
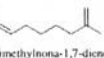
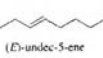
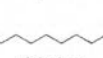
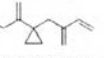
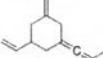
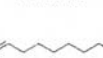
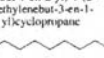
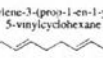


Figure 4.5 Total ion chromatogram with peak markers of OLEs classified based on carbon number.

Table 4.4 Examples of OLEs found in each carbon number

Carbon number	Hydrocarbon species of OLEs		
8	 (3E,5Z)-octa-1,3,5-triene	 (2Z,4Z)-3,4-dimethylhexa-2,4-diene	 (E)-2-methylhept-3-ene
9	 3,3-dimethylhepta-1,6-diene	 (E)-non-4-ene	 nona-1,2-diene
10	 (E)-3-ethyl-2-methylhepta-1,3-diene	 3,7-dimethyloct-1-ene	 (2E,8E)-deca-2,8-diene
11	 2,8-dimethylnona-1,8-diene	 2,8-dimethylnona-1,7-diene	 (E)-undec-5-ene
12	 dodec-1-ene	 1-(but-1-en-2-yl)-1-(2-methylenebut-3-en-1-yl)cyclopropane	 1-methylene-3-(prop-1-en-1-ylidene)-5-vinylcyclohexane
13	 (E)-tridec-3-ene	 (Z)-tetradec-3-ene	 (5E,9E)-tetradeca-1,5,9,13-tetraene

4.4.2.3 Terpenes (TERs)

The classification of TERs is evaluated from the isoprene present in the basic molecular skeleton (Stoessl *et al.*, 1976, Steele *et al.*, 1998), which are of the two classes, carenes and limonenes, as stated in Table 4.1. Moreover, TERs in the TDO can also be classified according to carbon number as illustrated in Figure 6. Examples of species in each class of carbon number are shown in Table 4.5.

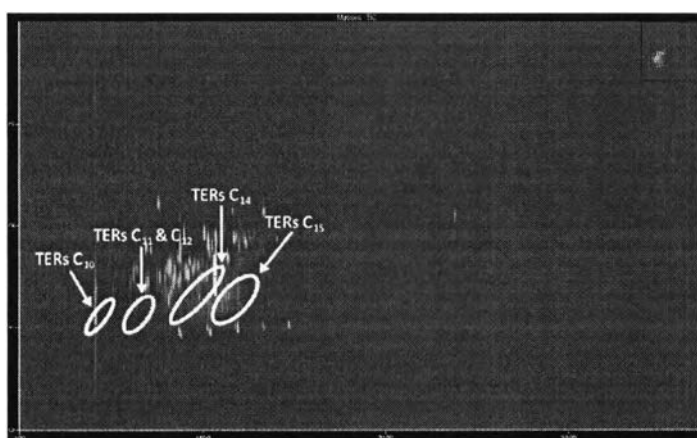
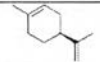


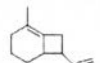
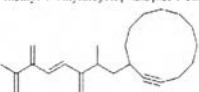
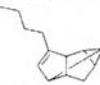

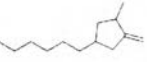
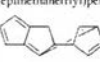
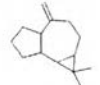

**Figure 4.6** Total ion chromatogram with peak markers of TERs classified based on carbon number.

Table 4.5 Examples of TERs found in each carbon number

Carbon number	Hydrocarbon species of TERs		
10	 (S)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene	 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene	 3-methyl-4-methylenebicyclo[3.2.1]oct-2-ene
11	 2-methyl-7-vinylbicyclo[4.2.0]oct-1-ene		
12	 (E)-3-(2,7-dimethyl-3,6-dimethylenoocta-4,7-dien-1-yl)cyclododec-1-yne		
13	 5-butyl-1,2,3,3a,4,6a-hexahydro-1,2,4-(epimethanetriyl)pentalene	 (Z)-bicyclo[10.1.0]tridec-1-ene	 Cyclopentene, 5-hexyl-3,3-dimethyl-
14	 1H-1,4,8-(epimethanetriyl)cyclopenta[flazulene		
15	 1,1-dimethyl-4-methylenedecahydro-1H-cyclopropa[e]azulene	 3,8-dimethyl-4-(prop-1-en-2-yl)-1,2,3,3a,4,5,8,8a-octahydroazulene	

4.4.2.3 Di-aromatics (DAHs)

The DAHs are hydrocarbons containing two benzene rings fused together, which are naphthalene and alkylnaphthenes (IUPAC, IUPAC). As a result, classified according to carbon number, DAHs in TDOs are composed of hydrocarbon species starting at C10 to C14. Figure 4.7 shows the classes of DAHs found in TDOs with peak markers: C10, C11, C12, C13 and C14 from left to right. Examples of species in each carbon number are shown in Table 4.6.

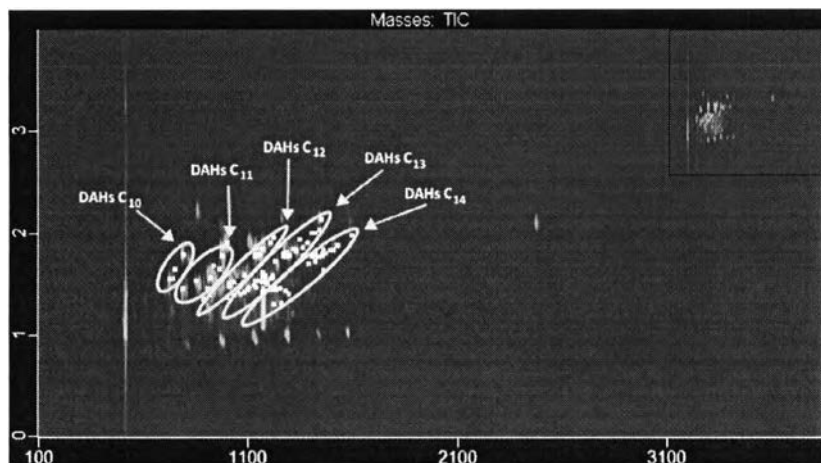












Figure 4.7 Total ion chromatogram with peak markers of DAHs classified based on carbon number.

Table 4.6 Examples of majority of DAHs found in each carbon number

Carbon number	Hydrocarbon species of DAHs		
10	 naphthalene		
11	 1-methylnaphthalene		
12	 1,2-dimethylnaphthalene	 2,7-dimethylnaphthalene	
13	 1-allylnaphthalene	 1-(prop-1-en-2-yl)naphthalene	 1,4,5-trimethylnaphthalene
14	 7-isopropyl-1-methylnaphthalene	 1,2,3,4-tetraethylnaphthalene	 2-butyl-naphthalene

4.4.2.4 Poly-aromatics (PAHs)

The PAHs contain three or more than two benzene rings fused together, which can be classified into anthracenes, pyrenes, phenanthrenes, and 1,1'-biphenyl. The mostly-found compounds in each class are shown in Table 4.1. The 1,1'-biphenyl is classified as a poly-aromatic hydrocarbon, although the two benzene rings do not fuse together, but form a new carbon-carbon bond (IUPAC, IUPAC). As a result, PAHs in TDOs contain hydrocarbon species starting at C12, C13, and C14 as shown in Figure 4.8 from left to right. Examples of species in each carbon number are shown in Table 4.7.

4.4.2.5 Polar-aromatics (PPAHs)

The polar-aromatic hydrocarbons (PPAHs) are aromatic hydrocarbons having at least two atoms of different elements in the benzene ring. For example, benzothiophene is composed of thiophene and benzene fused together. Moreover, when two benzene rings are fused together with thiophene, the compounds are called dibenzothiophenes. As a result, it is found that PPAHs in TDOs can be classified to hydrocarbon classes starting at C₉, C₁₀, C₁₁, and C₁₂ as shown in Figure 4.9 from left to right. Examples of species in each carbon number are shown in Table 4.8. The polar-aromatics in TDO are mostly sulfur-containing compounds.

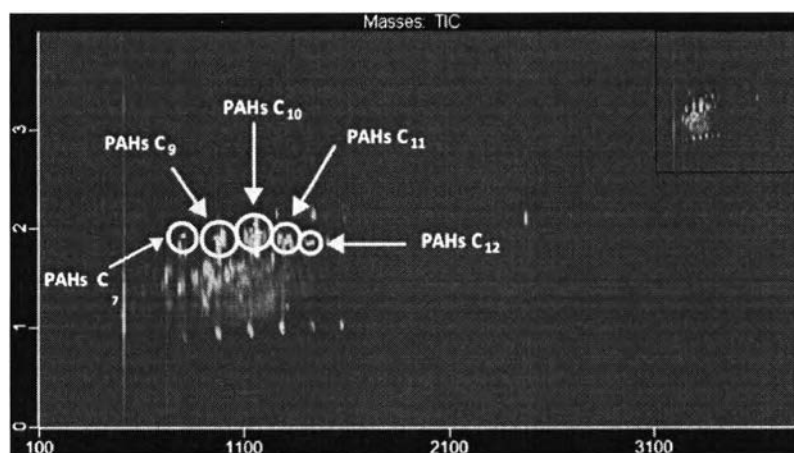

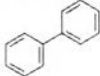
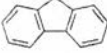
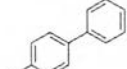
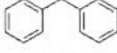

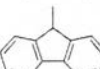
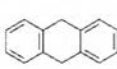


Figure 4.8 Total ion chromatogram with peak markers of PAHs classified based on carbon number.

Table 4.7 Examples of PAHs found in each carbon number

Carbon number	Hydrocarbon species of PAHs		
12	 1,2-dihydroacenaphthylene	 1,1'-biphenyl	
13	 9H-fluorene	 4-methyl-1,1'-biphenyl	 diphenylmethane
14	 (Z)-1,2-diphenylethene	 9-methyl-9H-fluorene	 9,10-dihydroanthracene

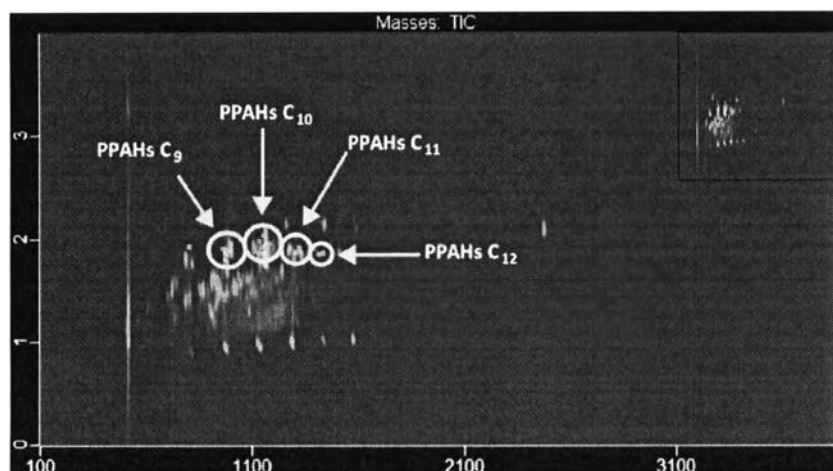


Figure 4.9 Total ion chromatogram with peak markers of PPAHs classified based on carbon number.

Table 4.8 Examples of PPAHs found in each carbon number

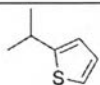
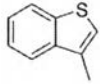
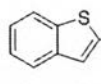
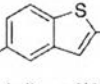
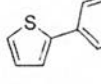
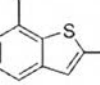
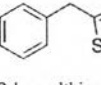
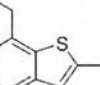
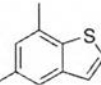
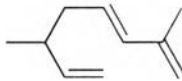



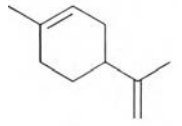
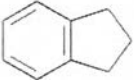
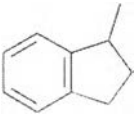
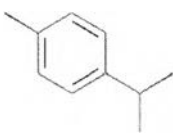
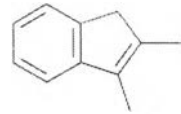
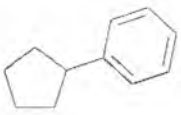
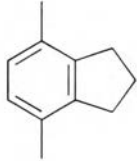
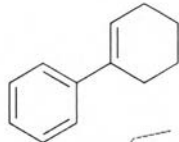
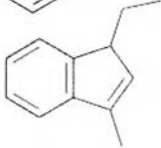

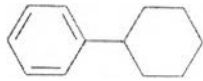
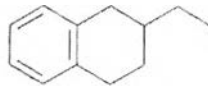
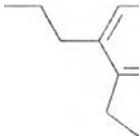

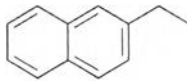
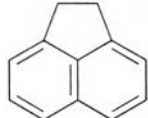
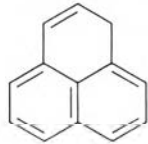
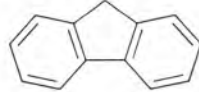
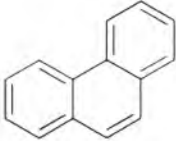
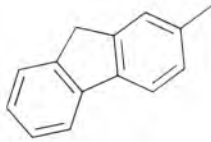
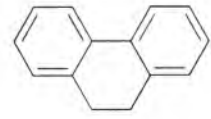
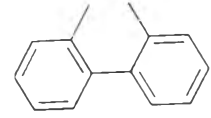
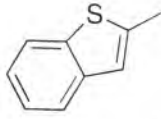
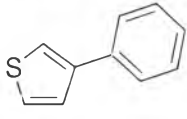
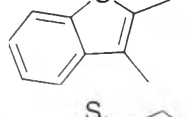
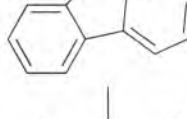
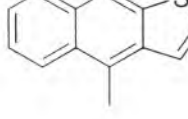
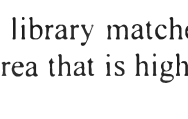
Carbon number	Hydrocarbon species of PPAHs
7	 2-isopropylthiophene
9	 3-methylbenzo[<i>b</i>]thiophene  2-methylbenzo[<i>b</i>]thiophene
10	 2,5-dimethylbenzo[<i>b</i>]thiophene  2-phenylthiophene
11	 7-ethyl-2-methylbenzo[<i>b</i>]thiophene  2-benzylthiophene
12	 2,7-diethylbenzo[<i>b</i>]thiophene  2-ethyl-5,7-dimethylbenzo[<i>b</i>]thiophene

Table 4.1 Abundantly-found hydrocarbons in tire-derived oils

Group	Carbon number	m/z^a	Assigned compound ^b	
SATs	13	184.219	Tridecane	$\text{CH}_3\left[\text{CH}_2\right]_{11}\text{CH}_3$
	14	198.235	Tetradecane	$\text{CH}_3\left[\text{CH}_2\right]_{12}\text{CH}_3$
	16	226.266	Hexadecane	$\text{CH}_3\left[\text{CH}_2\right]_{14}\text{CH}_3$
OLEs	10	136.125	Isomycorene	
	13	182.203	Tridecene	
	14	196.219	Tetradecene	
TERs	10	136.125	3-Carene	
			d-Limonene	
MAHs	9	118.087	Indane	
	10	132.094	1-ethylIndane	
		134.110	p-Cymene	
	11	144.094	2,3-dimethylIndene	
		146.110	Cyclopentylbenzene	

Group	Carbon number	m/z^a	Assigned compound ^b		
MAHs	11	146.110	4,7-dimethyl-2,3-dihydro-1H-Indene		
	12	158.110	Cyclohexenylbenzene		
			1-ethyl-3-methylIndene		
			hexa-2,4-dimethylBenzene		
		160.125	Cyclohexylbenzene		
			5-ethyl-1,2,3,4-Tetrahydroaphthalene		
			4-propyl-2,3-dihydro-1H-indene		
		162.141	Hexylbenzene		
	DAHs	12	156.094	2-ethylnaphthalene	
	PAHs	12	154.078	1,2-dihydroacenaphthylene	
13		166.078	1H-phenalene		
			9H-fluorene		

Group	Carbon number	m/z^a	Assigned compound ^b	
PAHs	14	178.078	Phenanthrene	
		180.094	9-methyl-9H-fluorene/	
		182.110	9,10-dihydrophenanthrene	
			2,2-dimethyl-1,1'-biphenyl	
PPAHs	7	126.050	Thiophene, 2-(1-methylethyl)-	
	9	148.035	Benzo[b]thiophene, 2-methyl-	
	10	160.035	Thiophene, 2-phenyl-	
		162.050	Benzo[b]thiophene, 2,5-dimethyl-	
	12	184.035	Dibenzothiophene	
		212.066	Naphtho[2,3-b]thiophene, 4,9-dimethyl-	

^aMass peak and ^bAssigned compound are based on the NIST library matches. The criteria used for identification hydrocarbon species are the %area that is higher than 0.1 % and match peaks that are more than 750.

4.5 Conclusions

It was succeeded to analyze the tire-derived oil by using GC × GC–TOF/MS processed by LECO ChromaTOF® software. The data processing can be done within 180 min. The chromatographic peaks were explicitly resolved. The hydrocarbon species found in the tire-derived oil were more than 1,500 compounds, and can be classified into groups of MAHs, SATs, OLEs, TERs, DAHs, PAHs, and PPAHs including sulphur compounds. As a result, MAHs were categorized into two groups: (a) mono-aromatics with saturated substituents (MAHs-SS) such as indanes, alkylbenzenes, and tetralins, and (b) mono-aromatics with unsaturated substituents (MAHs-US) such as indenenes and alkenylbenzene. The carbon number of SATs ranged between C13 to C16. OLEs were di-olefins and tri-olefins with C8-C14. TERs were classified into 3-carene and d-Limonene found to have carbon numbers in the range of C10-C15. DAHs consisted of naphthalene and alkyl-naphthalenes with C10-C14. PAHs contained phenanthrenes, anthracenes, fluorenes, and pyrenes, with C12-C14. Finally, PPAHs consisted of thiophenes, benzothiophenes, and dibenzothiophenes with C9-C12.

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