

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

**5.1 Abstract**

A tire-derived oil (TDO) consists of various sulphur compounds. Previously, a GC/MS has been used to analyze the sulphur compounds in TDOs, and 10 sulphur compounds were found and identified. However, the drawback of a regular GC/MS is that it cannot separate the sulphur compounds eluted at the same retention time because boiling points, vapor pressures and mass spectral fragmentation patterns are indistinguishable. At present, no analysis of sulphur compounds in a TDO using Two-Dimensional Gas Chromatography coupled with a Time-of-Flight Mass Spectrometry (GC x GC / TOF-MS) has been reported. The objective of this work was thus to examine the sulphur compounds in a TDO using a GC x GC / TOF-MS, and report the results in 2D (contour) and 3D (surface) plots of total ion chromatograms for analyzing and grouping of sulphur compounds based on carbon number. As a result, the S-compounds with C7–C11 consisted of thiophenes, benzothiophenes, and their derivatives, whereas those of C12–C13 consisted of C12-benzothiophenes, dibenzothiophenes, and their derivatives. Finally, the C14 S-compounds were the combination of dibenzothiophenes and phenalenothiophenes. Furthermore, detected by GC x GC / TOF-MS, phenalenothiophenes was the new group of S-compounds found in the TDO.

Keywords: Tire-derived oil, GC × GC – TOF/MS, Sulphur compounds, Grouping

**5.2 Introduction**

Tire-derived oil (TDO) contains approximately 0.8 – 1.1 % wt sulphur (Roy *et al.*, 1990; William *et al.*, 1995). The S-compounds in TDO may give rise to toxic and corrosive SO<sub>x</sub>. Moreover, S-compounds are a group of refractory compounds

that need a specific process for treatment, like hydrodesulfurization (HDS). Several studies showed that the reactivity of S-compounds in HDS decreased in the order: thiophenes > benzothiophenes > dibenzothiophenes > alkyldibenzothiophene (Kilanowski *et al.*, 1978; Houalla *et al.*, 1980; Andari *et al.*, 1996). For the alkyldibenzothiophenes, 2,8-dimethyldibenzothiophene was more reactive than 4-methyldibenzothiophene. The one with the lowest reactivity in the alkylbenzothiophenes is 4,6-dimethyldibenzothiophene due to steric hindrance (Andari *et al.*, 1996; Gutiérrez and Klimova, 2011). Therefore, the structure of S-compounds in TDO should be accounted for, in consideration of the reactivity in HDS.

William and Brotrill (1995) studied the sulphur-polycyclic aromatic hydrocarbons in tire pyrolysis oil. They used liquid column chromatography to separate sulfur-polycyclic aromatic hydrocarbons and that were then analyzed by using a normal GC/MS. They found that 10 S-compounds existed in TDO; however, the chromatograms were not explicitly resolved. Moreover, Lagesgoiti *et al.*, (2004) characterized the components 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. In conclusion, it is not easy to resolve overlapped peaks from the 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 × GC- TOF/MS) is a new technique that has high performance to resolve the complexity of compounds. In terms of 2D, two consecutively-connected columns are employed with a 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 and Beens, 1999). Time-of-

flight (TOF/MS) instrument is able to scan at the high scan rates of  $\geq 50$  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). Equipped with a software that can deconvolute chromatograms for identification as well as accurate quantification (Marriott and Shellie, 2002). the raw data can be 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. 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 using this technique (Dallüge *et al.*, 2002. Nelson *et al.*, 2006, Melbye *et al.*, 2009, Manzano and Simonich, 2012).

At present, no analysis and grouping of S-compounds in a TDO using GC x GC / TOF-MS have been reported. The objective of this work was, thus, to examine the S-compounds in a TDO using a GC x GC / TOF-MS, and report the results in 2D (contour) and 3D (surface) plots of total ion chromatograms for analyzing and grouping of S-compounds based on carbon number.

## 5.3 Experimental

### 5.3.1 Pyrolysis of Waste Tire

The pyrolysis experiment was conducted using the system described in (Düng *et al.*, 2009). 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<sup>-1</sup>, and kept at the final temperature for one hour to ensure the total conversion of tire. A 25 ml min<sup>-1</sup> 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.

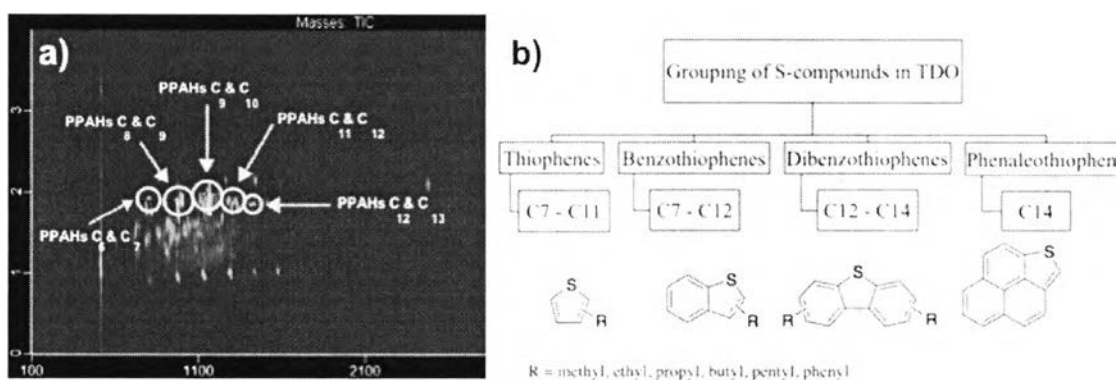
### 5.3.2 Analysis Using GC × GC – TOF/MS

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<sup>-1</sup> 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<sup>-1</sup> with 10 minute holding at the final temperature. One µl of the 10 mg/ml maltenes in carbondisulfide (CS<sub>2</sub>) 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.

## 5.4 Results and Discussion

### 5.4.1 S-compounds in tire-derived oil using 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. In Figure 5.1(a), the contour plot indicates the S-compounds in tire-derived oil, which are explicitly separated from each other in the same group of carbon number. It indicates that the conditions used to analyze the tire-derived oil are satisfied to separate the complex components as well. As a result, the S-compounds in the tire-derived oil are in the range of C7 – C14 as shown in Figure 5.1(a).



**Figure 5.1** a) grouping of S-compounds based on carbon number and b) classification of S-compounds in a tire-derived oil obtained from the non-catalyst batch.

### 5.4.2 Grouping of S-compounds in the Tire-derived Oil

According to the IUPAC, the aromatic heterocyclic compounds or so-called polar-aromatic hydrocarbons (PPAHs) are aromatic hydrocarbons having at least two atoms of different elements in the benzene ring (IUPAC, 1979). This work focuses only on the classification of sulphur atoms in PPAHs. Figure 5.1(b) shows

the classification of S-compounds found in the TDO. The S-compounds are categorized into four classes according to their chemical structure; that are, thiophenes, benzothiophenes, dibenzothiophenes, and phenalenothiophenes. The new, distinguished class of S-compounds, that is phenalenothiophenes, was found using GC × GC – TOF/MS.

#### *5.4.2.1 Thiophenes*

Thiophenes are composed of thiophene and derivatives. The substituents can be alkyl or phenyl. The class of thiophenes is categorized according to carbon number. As a result, they start at C7 to C11. The examples of C7 – C11 thiophenes are shown in Table 5.1.

#### *5.4.2.2 Benzothiophenes*

Benzothiophenes are composed of thiophene and a benzene ring fused together. Benzothiophene derivatives are different at the substituents. Benzothiophenes are also categorized based on carbon number. As a result, they range from C8 to C12. The examples of C8 – C12 benzothiophenes are shown in Table 5.1.

#### *5.4.2.3 Dibenzothiophenes*

Dibenzothiophenes are composed of thiophene and two benzene rings fused together with thiophene in between the two benzene rings. Dibenzothiophene derivatives are different at the substituents. Dibenzothiophenes are categorized based on carbon number as well. As a result, they range from C12 to C14. The examples of C12 – C14 dibenzothiophene are shown in Table 5.1.

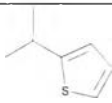
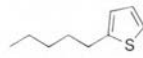
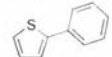
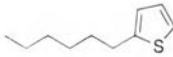
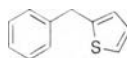





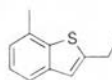
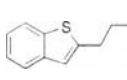
#### *5.4.2.4 Phenalenothiophenes*

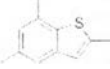
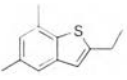
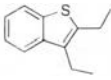

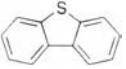
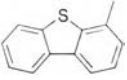
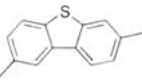
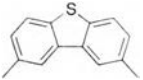
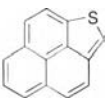
Phenalenothiophenes are composed of thiophene and 1H-phenalene fused together. Categorized by using carbon number, phenalenothiophene is present at individual C14, and has no derivative. The structure of phenalenothiophene is shown in Table 5.1.

## 5.5 Conclusions

It was succeeded to analyze S-compounds in 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 of S-compounds were explicitly resolved. Twenty-two S-compounds were found in the tire-derived oil, and can be classified into four classes: thiophenes, benzothiophenes, dibenzothiophenes, and phenalenothiophenes. Moreover, each class was also categorized based on carbon number. As a result, the S-compounds with C7–C11 consisted of thiophenes, benzothiophenes, and their derivatives, whereas those of C12–C13 consisted of C12-benzothiophenes, dibenzothiophenes, and their derivatives.

**Table 5.1** S-compounds in tire-derived oil

Class	Carbon number	Assigned compounds	
Thiophenes	7		
		2-isopropylthiophene	
	9		
		2-pentylthiophene	
	10		
	2-phenylthiophene	2-hexylthiophene	2-butyl-5-ethylthiophene
	11		
		2-benzylthiophene	
Benzothiophenes	8		
		benzo[ <i>b</i> ]thiophene	
	9		
		3-methylbenzo[ <i>b</i> ]thiophene	
	10		
	7-ethylbenzo[ <i>b</i> ]thiophene	3,5-dimethylbenzo[ <i>b</i> ]thiophene	
			
		2,7-dimethylbenzo[ <i>b</i> ]thiophene	
	11		
		2-ethyl-7-methylbenzo[ <i>b</i> ]thiophene	2-propylbenzo[ <i>b</i> ]thiophene

Class	Carbon number	Assigned compounds
Benzothiophene	11	 2,5,7-trimethylbenzo[ <i>b</i> ]thiophene
	12	 2-ethyl-5,7-dimethylbenzo[ <i>b</i> ]thiophene  2,3-diethylbenzo[ <i>b</i> ]thiophene
		 2,7-diethylbenzo[ <i>b</i> ]thiophene
Dibenzothiophenes	12	 dibenzo[ <i>b,d</i> ]thiophene
	13	 4-methyldibenzo[ <i>b,d</i> ]thiophene
	14	 2,7-dimethyldibenzo[ <i>b,d</i> ]thiophene  2,8-dimethyldibenzo[ <i>b,d</i> ]thiophene
Phenalenothiophenes	14	 phenaleno[1,9- <i>bc</i> ]thiophene

Finally, the C<sub>14</sub> S-compounds were the combination of dibenzothiophenes and phenalenothiophenes. Furthermore, detected by GC x GC / TOF-MS, phenalenothiophenes was the new group of S-compounds found in the TDO.

## 5.6 Acknowledgements

The following agencies are acknowledged for their mutual financial support: The Thailand Research Fund (TRF) and Center of Excellence on Petrochemical and Materials Technology.



## 5.7 References

- Andari, M.K., Abu-Seedo, F., Stanislaus, A. and Qabazard, H.M. (1996). Kinetics of individual sulfur compounds in deep hydrodesulfurization of Kuwait diesel oil. *Fuel*, 75(14), 1664-1670.
- Dallüge, J., van Stee, L.L.P., Xu, X., Williams, J., Beens, J., Vreuls, R.J.J. and Brinkman, U.A.T. (2002). Unravelling the composition of very complex samples by comprehensive gas chromatography coupled to time-of-flight mass spectrometry: Cigarette smoke. *Journal of Chromatography A*, 974(1–2), 169-184.
- Dallüge, J., Vreuls, R.J.J., Beens, J. and Brinkman, U.A.T. (2002). Optimization and characterization of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection (GC×GC–TOF MS). *Journal of Separation Science*, 25(4), 201-214.
- Dũng, N.A., Wongkasemjit, S. and Jitkarnka, S. (2009). Effects of pyrolysis temperature and Pt-loaded catalysts on polar-aromatic content in tire-derived oil. *Applied Catalysis B: Environmental*, 91(1–2), 300-307.
- Girgis, M.J., Gates, B.C. (1991) Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing. *Ind. Eng. Chem.*, 30, 2021.
- Gutiérrez, O.Y. and Klimova, T. (2011). Effect of the support on the high activity of the (Ni)Mo/ZrO<sub>2</sub>–SBA-15 catalyst in the simultaneous hydrodesulfurization of DBT and 4,6-DMDBT. *Journal of Catalysis*, 281(1), 50-62.
- International Union of Pure and Applied Chemistry, (1997). *Arenes*, IUPAC: Compendium of Chemical Terminology. Research Triangle Park: NC.
- Kilanowski, D.R., Teeuwen, H., De Beer, V.H.J., Gates, B.C., Schuit, B.C.A., Kwart, H. (1978) Hydrodesulfurization of thiophene, benzothiophene, dibenzothiophene, and related compounds catalyzed by sulfided CoO–MoO<sub>3</sub>/□-Al<sub>2</sub>O<sub>3</sub>: low-pressure reactivity studies. *J. Catal.*, 55, 129
- Laresgoiti, M.F., Caballero, B.M., de Marco, I., Torres, A., Cabrero, M.A. and Chomón, M.J. (2004). Characterization of the liquid products obtained in tyre pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 71(2), 917-934.

- Manzano, C., Hoh, E. and Simonich, S.L.M. (2012). Improved Separation of Complex Polycyclic Aromatic Hydrocarbon Mixtures Using Novel Column Combinations in GC × GC/ToF-MS. *Environmental Science & Technology*, 46(14), 7677-7684.
- Marriott, P. and Shellie, R. (2002). Principles and applications of comprehensive two-dimensional gas chromatography. *TrAC Trends in Analytical Chemistry*, 21(9–10), 573-583.
- Melbye, A.G., Brakstad, O.G., Hokstad, J.N., Gregersen, I.K., Hansen, B.H., Booth, A.M., Rowland, S.J. and Tollefsen, K.E. (2009). Chemical and toxicological characterization of an unresolved complex mixture-rich biodegraded crude oil. *Environmental Toxicology and Chemistry*, 28(9), 1815-1824.
- Nelson, R.K., Kile, B.M., Plata, D.L., Sylva, S.P., Xu, L., Reddy, C.M., Gaines, R.B., Frysiner, G.S. and Reichenbach, S.E. (2006). Tracking the Weathering of an Oil Spill with Comprehensive Two-Dimensional Gas Chromatography. *Environmental Forensics*, 7(1), 33-44.
- Phillips, J.B. and Beens, J. (1999). Comprehensive two-dimensional gas chromatography: a hyphenated method with strong coupling between the two dimensions. *Journal of Chromatography A*, 856(1–2), 331-347.
- Roy, C., Labrecque, B. and de Caumia, B. (1990). Recycling of scrap tires to oil and carbon black by vacuum pyrolysis. *Resources, Conservation and Recycling*, 4(3), 203-213.
- Williams, P.T. and Bottrill, R.P. (1995). Sulfur-polycyclic aromatic hydrocarbons in tyre pyrolysis oil. *Fuel*, 74(5), 736-742.