CHAPTER V
CHARACTERIZATION OF PRODUCTS DERIVED FROM THE PYROLYSIS OF DIFFERENT RAW MATERIALS

5.1 Abstract

In this study, pyrolysis of polyethylene (PE), polypropylene (PP), polystyrene (PS), waste tire (WT), sewage sludge (SS) and oil sludge (OS) was carried out in a fixed-bed reactor at 550°C. The results showed that the pyrolytic product yields, i.e. gas, liquid and solid, correspond to the composition obtained from proximate analysis. Most of volatile matters in raw materials are converted into gas and liquid fractions whilst fixed carbon and ash result in the solid product. The gas and liquid yields are up to 89 wt.% for the pyrolysis of PE, PP and PS because of their relatively high volatile matters whereas the solid yields are up to 62 wt.% for the pyrolysis of WT, OS and SS with respect to their high values of fixed carbon and ash content. Regardless of raw materials used, the composition of the gaseous products is insignificantly different and mainly composed of H_2, and C_1-C_4 hydrocarbons. On the other hand, the composition of liquid products consisting of water, oil, and wax is varied dependently on the nature of raw materials. The characteristics of pyrolytic oils were found to be varied and influenced by the chemical structures of the starting materials containing aliphatic, aromatic, oxygenated and nitrogenated groups.

5.2 Introduction

Pyrolysis of waste materials has been received a great attention since the pyrolytic liquid or bio-oil has high potential to be used as fuels or other useful chemicals. Comprehensive reviewing articles on biomass pyrolysis science and technology including pyrolytic liquid applications have been published [1-5]. The yields and compositions of pyrolytic oils are influenced by not only the reactor types and pyrolysis conditions [6, 7] but also the chemical structures of the pyrolyzed materials. For instance, oils from the simple structures of polyolefin wastes such as polyethylene (PE) and polypropylene (PP) yield the oil and wax that are mainly composed of alkanes, alkenes and alkadienes [8]. Pyrolysis of polystyrene (PS) was reported to produce the

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pyrolytic liquid having styrene and other aromatics as main products [9]. Although waste tires (WT) are a complex mixture of rubbers, steel cord, and other minor components, the pyrolytic liquid obtained from their pyrolysis mainly contains single ring aromatics (such as benzene, toluene and xylenes) and dipentenes (or limonene) [10]. For highly heterogeneous materials, e.g. sewage sludge (SS) and oil sludge (OS), the obtained pyrolytic liquids from them present somewhat complex compositions. The oxygenated aromatic compounds of phenols and their derivatives and long chain aliphatic carboxylic acids are the dominating components in the oil from sewage sludge [11]. For liquids derived from oil sludge, the aliphatics and aromatics are their major compositions [12]. In this contribution, the pyrolysis of several types of materials such as PE, PP, PS, WT, SS and OS was investigated in a fixed bed reactor at 550°C. The pyrolytic products were then characterized by various techniques. The relationships between raw material composition and pyrolytic product yield were determined. In addition, an attempt in correlating the chemical structure of raw materials and component of products has been made.

5.3 Experimental

5.3.1 Materials

To study the effects of chemical structures of feedstocks on the composition of pyrolytic oil, polyethylene (PE), polypropylene (PP), polystyrene (PS), waste tire (WT), sewage sludge (SS) and oil sludge (OS) were chosen. According to their building unit and the hydrogen to carbon ratio (H/C atomic ratio), these materials were categorized into 3 groups, aliphatic, aliphatic + aromatic, and complex aliphatic + aromatic compounds, as shown in Table 5.1. PE was selected as a representative for the aliphatic structure while PS was for both the aliphatic and aromatic structures. Similar to PE, PP contains the aliphatic structure but it also contains methyl group on the side of backbone. Hence, PP was justified to be an intermediate structure between PE and PS. Furthermore, similar to PS, WT contains both the aliphatic and aromatic structures but it contains much lower aromatic content. The SS and OS were categorized as highly heterogeneous materials due to their unknown building units. For SS, there are attempts to illustrate a similarity between their compositions and those of the biomass fractions [13].

Table 5.1 Classification of pyrolyzed materials

Material	Building unit	Elemental composition	Category
Polyethylene	Ethylene	C, H	Aliphatics
Polypropylene	Propylene	C, H	Aliphatics[a]
Polystyrene	Styrene	C, H	Aliphatics + aromatics
Tire[b]	Styrene-co-butadiene, isoprene	C, H, O, N, S	Aliphatics + aromatics
Sewage sludge	Lignocellulosic, lipids and proteins	C, H, O, N, S	Complex aliphatics + aromatics
Oil sludge	Heavy hydrocarbon compound	C, H, O, N, S	Complex aliphatics + aromatics

[a] intermediate structure between PE and PS

[b] lower aromatic contents compared to PS

5.3.2 Pyrolysis

The experiments were performed in a gas-distributed fixed-bed pyrolyzer. About 50 g of a sample was placed in a wired-mesh basket hung over a gas-distributor installed in a 2.5 L stainless steel reactor and heated by an electric furnace. The reactor was purged prior to the experiment by flowing N_2 to eliminate air originally contained in the reactor. The N_2 flow rate was then increased to 100 ml min^{-1} while the reactor temperature was increased from room temperature to 550°C with a heating rate of 20°C min^{-1}. The swept-out volatile containing products were condensed in a series of cold traps maintained at below 0°C with the aid of an ice/acetone mixture.

5.3.3 Products analysis

Pyrolytic gases were chromatographically analyzed using a Shimadzu GC 8A fitted with a thermal conductivity detector (TCD). A CTR I (Alltech) packed column was used to separate the gases under isothermal condition at 50°C. The temperatures of both injector and detector were set at 120°C.

Pyrolytic oils obtained from each experiment were dissolved in a mixture of n-pentane to methanol volume ratio of 1:1. Then, the deuterated standards, benzene-d_6, naphthalene-d_8, phenanthrene-d_{10} and octadecanoic acid-d_{35}, were added into the solution prior to the analysis by using a ThermoFinnigan Trace GC 2000 gas chromatograph connected with a PolarizQ mass spectrometer (GC-MS). One μL resultant solution was injected into a 250°C-injection port with the splitless injection

mode. A ZB-5 capillary column of 60 m×0.25 mm coated with a 0.25 μm thick film of 5% phenylmethylpolysiloxane was equipped at the injection port with flowing He of 1.0 ml min^{-1} under the programmed oven temperature. Initially, the GC oven was set at 40°C and held for 7 min then increased to 300°C with a heating rate of 5°C min^{-1}, and maintained at 300°C for 30 min. The MS was operated at an electron energy of 70 eV in electron impact ionization mode. Data were collected in a full scan mode with the m/z ratios between 10 and 250. The chromatographic peaks, with signal to noise ratio greater than 500, were identified using the NIST spectrum library. A semiquantitative estimation of the yields was determined using the corresponding factors obtained from the deuterated standards.

5.4 Results and Discussion

5.4.1 Product yields

Table 5.2 shows the proximate analysis, elemental composition of starting materials, and product distribution obtained from pyrolysis of such materials. It was found that PE, PP and PS have volatile matters as a main fraction while WT, SS and OS contain less volatile but more fixed carbon and ash. The ultimate analysis showed that PE, PP and PS consist solely of C and H, while the presence of heteroatoms such as O, N and S was found in WT, SS and OS in particular for SS and OS. Similar proximate and ultimate analyses were also reported in the other literatures [14-17].

Generally, pyrolysis products consist of gas, liquid and solid products. As shown in Table 5.2, liquid (up to 89 wt.%) is the major product obtained from pyrolysis of PE, PP and PS while solid (up to 62 wt.%) is the main pyrolytic product of WT, SS and OS. The gas yield was found in the range of ca. 9 to 18 wt.%. The results suggested that the more the volatile matters, the higher the gas and liquid fractions, on the other hand, the less the volatile matters, the higher the solid fraction. The solid yields of such materials were observed to be higher than the combination of fixed carbon and ash in the starting materials. It was, in turn, suggested that not only be the solid residue generated from the fixed carbon and ash but also be derived from polymerization and carbonization of pyrolytic products [18].

Liquids derived from pyrolysis of plastics (PE, PP and PS) consist of oil (ca. 43-70 wt.%) and wax (ca. 19-38 wt.%). It was noticed that the wax content is related to

the aliphatic content of raw materials since both PE and PP contain considerable amounts of aliphatic content (Table 5.2). In pyrolysis, PP yielded lower wax fraction than PE because PP contains methyl pendant groups which can be converted into more oil product [9]. The high amount of water produced is expected from the materials containing high oxygen contents [19]. For example, WT contains only 3.4 wt.% oxygen and then yields 1.1 wt.% water in total pyrolytic product while SS and OS containing oxygen more than 40 wt.% provide water of 12 wt.% or higher.

Table 5.2 Proximate analysis, elemental composition of starting materials, and product distribution obtained from pyrolysis of such materials.

Material	PE	PP	PS	WT	SS	OS
Proximate analysis (wt.%)						
Volatile	99.97	99.2	99.8	62.2	43.4	48.1
Fixed carbon	-	0.11	-	29.4	5.2	11.0
Ash	0.03	0.70	0.2	7.1	46.3	38.4
Elemental composition (wt.%)						
C	85.7	85.7	92.3	86.4	42.0	48.8
H	14.3	14.3	7.7	8.0	6.8	7.1
O	-	-	-	3.4	41.5	43.3
N	-	-	-	0.5	6.4	0.8
S	-	-	-	1.7	3.3	2.4
Distribution of products (wt.%)						
Gas[a]	17.4	17.7	8.9	18.2	13.5	15.8
Liquid[b]	81.3	80.8	88.9	36.5	24.7	32.2
Oils	43.1	52.7	70.0	28.1	11.9	20.2
Wax	38.2	27.1	18.9	7.3	-	-
Water	-	-	-	1.1	12.8	12.0
Solid	1.3	1.5	2.2	45.3	61.8	52.0
Oils/Wax ratio	1.1	2.3	3.7	3.8	-	-
Oils/Water ratio	-	-	-	25.5	0.9	1.7

[a] wt.% gas = 100 − wt.% oil − wt.% wax − wt.% water − wt.% solid

[b] wt.% liquid = wt.% oils + wt.% wax + wt.% water

5.4.2 Gas and oil compositions

Table 5.3 shows the compositions of gaseous products derived from the fixed-bed pyrolysis of each raw material. Typically, they are composed of hydrogen, C_1-C_4 hydrocarbons, CO and CO_2. Methane was found as the main composition in gaseous products obtained from PE, PP, PS and WT whereas CO and CO_2 were the main compositions of gaseous products from OS and SS pyrolysis. Since CO and CO_2 are produced from the materials containing oxygen when pyrolyzed. CO was produced by decarbonylation and CO_2 was produced by decarboxylation [20]. Another possible explanation for CO production is that the resulting CO_2 can further react with the char formed during the pyrolysis, and then produce CO via char gasification reaction [19].

Table 5.3 Gaseous products obtained from pyrolysis of such materials.

Composition	Material					
	PE	PP	PS	WT	SS	OS
Gas yield (wt.%)						
Hydrogen	0.22	0.41	1.30	0.67	0.78	1.04
Methane	7.57	9.05	3.86	7.93	0.69	0.66
Ethane	2.74	2.55	1.31	0.93	0.06	0.28
Ethylene	2.82	2.48	2.07	2.10	0.10	0.34
$C_3 + C_4$	4.05	3.21	0.36	2.89	0.99	0.79
Carbon monoxide	-	-	-	0.30	2.01	2.48
Carbon dioxide	-	-	-	3.38	8.87	10.21
Total (wt.%)	17.4	17.7	8.9	18.2	13.5	15.8

The chromatograms and the compositions of pyrolytic oils derived from each raw material are depicted in Figure 5.1 and summarized in Table 5.4, respectively. The results showed that oil compositions can be divided into 4 main groups; (*i*) aliphatics which can be divided into 3 subgroups as alkanes, alkenes and alkadienes, (*ii*) single ring aromatics and its alkyl derivatives, (*iii*) oxygenates and (*iv*) nitrogenates. It was observed that aliphatics exist in the oils derived from the materials containing mainly the aliphatic structures, such as PE and PP, whilst aromatics contain in those derived from the materials having the aromatic structures, such as PS, WT, SS and OS.

Oxygenates and nitrogenates were found only in the oils derived from the materials that contain heteroatoms of O and N, respectively, such as WT, SS and OS. Sulfur containing compounds were, on the other hand, not found in all derived oils. This might be due to the pyrolytic oils contain only a little amount of sulfur containing compounds which cannot be detected by MS with S/N (signal to noise) ratios > 500. Another possibility is it might be trapped by the solid residue formed during the course of reactions. However, it was reported that approximately half of the original sulfur still remained in the solid char rather than being released as a vapor during pyrolysis in the range of 350-850°C [21].

A wide range of product distribution was expected from the thermal degradation of the polyalkene plastics (*i.e.*, PE and PP) because a pyrolysis reaction was believed to occur through the random scission mechanism [22]. PE pyrolysis normally yields a board distribution of aliphatic products consisting of alkadienes, 1-alkenes and *n*-alkanes (Figure 5.1(a)). Since the proportion of alkadienes was present in a small fraction, it might be due to alkadienes were converted into 1-alkenes and n-alkanes by self-hydrogenation reaction [8].

Because PE and PP are similar in their structure, the thermal degradation products would be anticipated to be similar. However, the product distribution (Figure 5.1(b)) and oil composition (Table 5.4) of those derived from both PE and PP pyrolysis are somewhat different. The main compositions in the oil obtained from PP pyrolysis are the saturated alicyclic hydrocarbons such as 1,3,3,-Trimethyl-2-cyclohexane and 3-Ethyl-5-methyl cyclohexane. The saturated and unsaturated branched hydrocarbons were also found in significant amounts, such as 5-Tridecene and 2-Methyl octene. This might be due to the methyl group at the PP hydrocarbon backbone which can influence the selectivity toward alicyclic and branched hydrocarbons resulted from the radical recombination [9].

Styrene was also reported as the main product for PS derived oil [23-25]. In this study, as shown in Figure 5.1(c), styrene and its oligomers were produced up to ca. 64 wt.%. The chain scission preferentially takes place at the C-C bonds pertaining to the backbone rather than at others *e.g.*, C-C conjugated bonds in the phenyl group. This leads to the formation of the styrene monomer. Subsequently, styrene can further react to form styrene oligomers and other hydrocarbons such as toluene, methylbenzene and a series of aliphatic products [23].

Besides the known primer structures (*i.e.*, PE, PP and PS), the analyses of the oils derived from multi-primer structures of waste tire (WT), sewage sludge (SS) and oil sludge (OS) were carried out. The resultant chromatograms are shown in Figures. 5.1(d), 5.1(e) and 5.1(f), respectively. The WT derived oil contains the highest amount of *d*-limonene (up to 12 wt.%) and various amounts of unsaturated compounds such as 4-propyl-3-heptene, 5,8-diethyl dodecene, 2,6,10-trimethyl dodecene and 2,6,10-trimethyl tetradecene. The similar finding was also reported elsewhere [26]. *d*-Limonene was possibly generated by either the depolymerization of natural rubber through *β*-scission [27] or isoprene monomer recombination via a Diels-Alder reaction [28]. Moreover, phenols and acids were also found. These are the degradation products of oxygenated compounds containing in the tire additives, such as stearic acid and extender oil [26].

The SS consists of several organic and inorganic compounds. Cellulose, hemicellulose, lignin, fats, oils and proteins are the main organic constituents in SS [13]. In SS pyrolysis, the obtained oil compositions were somewhat complex and they consist of aliphatics (20 wt.%), single ring aromatics (7 wt.%), oxygenates (38 wt.%), and nitrogenates (14 wt.%). Moreover, some of *n*-alkanes and 1-alkenes were known to form by thermal degradation of acids and alcohols containing in SS [29]. The single ring aromatics and oxygenates were the products of the lignocellulosic compounds decomposition [11]. Fatty acids (particularly, long straight chain fatty acids) and steroids were present and originated from the sludge lipids. In addition, nitrogenated compounds (such as indole, trimethyl adenine) were generated from proteins which are initially in SS [30]. However, some unexpected products such as polycyclic aromatic hydrocarbons might be originated from the secondary pyrolysis reaction catalyzed by the metals in the sludge and char formed during the process.

Thermal decomposition of oil sludge (OS) yielded the aliphatic compounds as the major composition in oil fraction similar to that derived from PE. Apparently, the primer structure of the OS was mainly aliphatic-like compounds as indicated Table 5.4. However, single ring aromatic and oxygenated compounds were also found in its oil fraction. This can be attributed to the aromatization of the decomposed products leading to the formation of aromatics [31]. Similarly, the oxygenated compounds of ca. 5 wt.% might be originated from oxygen content in OS.
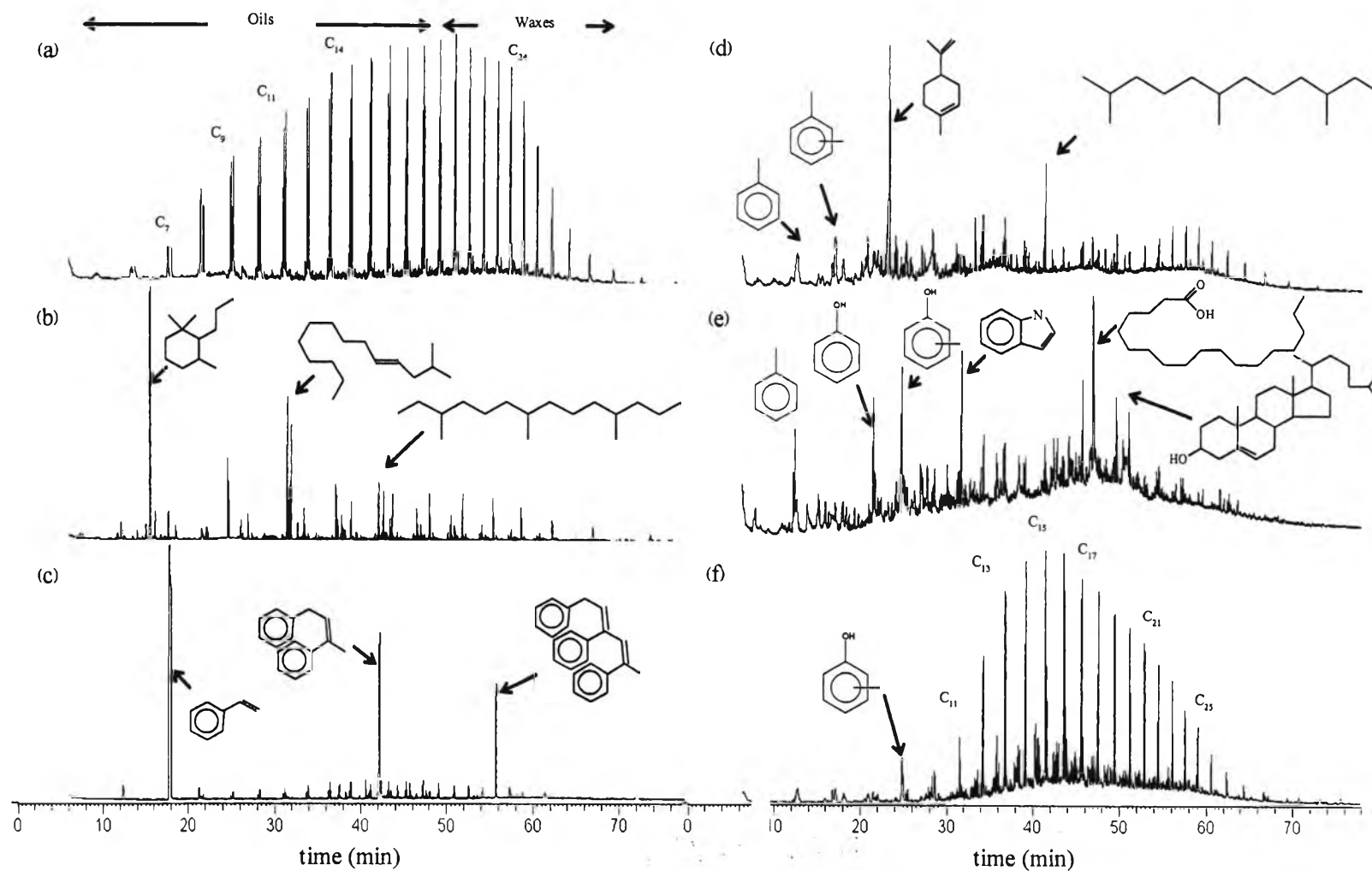
Figure 5.1 Total ion current chromatograms of oils derived from (a) polyethylene (PE), (b) polypropylene (PP), (c) polystyrene (PS), (d) waste tire (WT), (e) sewage sludge (SS), and (f) oil sludge (OS)

Table 5.4 Major components in pyrolytic oils derived from various materials

Material	Compound	wt.%	Compound	wt.%
Polyethylene	**Aliphatics**		**Aliphatics**	
(PE)	$n\text{-}C_6^a$	0.43	$n\text{-}C_{18}$	4.37
	$n\text{-}C_7$	0.76	$n\text{-}C_{19}$	4.41
	$n\text{-}C_8$	1.56	$n\text{-}C_{20}$	4.34
	$n\text{-}C_9$	1.75	$n\text{-}C_{21}$	4.21
	$n\text{-}C_{10}$	1.95	$n\text{-}C_{22}$	3.98
	$n\text{-}C_{11}$	2.01	$n\text{-}C_{23}$	3.96
	$n\text{-}C_{12}$	2.43	$n\text{-}C_{24}$	3.91
	$n\text{-}C_{13}$	2.64	$n\text{-}C_{25}$	3.01
	$n\text{-}C_{14}$	3.01	$n\text{-}C_{26}$	2.42
	$n\text{-}C_{15}$	3.81	$n\text{-}C_{27}$	1.48
	$n\text{-}C_{16}$	4.23	$n\text{-}C_{28}$	1.02
	$n\text{-}C_{17}$	4.36	$n\text{-}C_{29}^a$	0.75
			Unidentified	33.20
Polypropylene	**Aliphatics**		**Aliphatics**	
(PP)	3,4-Diethyl-3-hexane	0.91	5-Tridecene	3.25
	1,1,3-Trimethyl-2-cyclohexane	3.19	2,4,6-Trimethyl cyclohexane	2.74
	1,3,3-Trimethyl-2-cyclohexane	13.65	6,10-Dimethyl-1,6-diene dodecane	1.58
	1,3,5-Trimethyl cyclohexane	1.22	3,7,11-Trimethyl dodecane	1.34
	1-Heptene	1.04	i-Tridecane	1.32
	1-Butyl-2-ethyl-cyclopentane	1.27	2-Hexyl octene	0.62
	1,1-Dimethyl-2,4-diisopropyl	1.18	Tetradecene	1.22
	cyclohexane	2.00	3-Hexyl decene	1.83
	2-Methyl octene	2.73	2-Methyl-E-7-hexadecene	1.34
	1-Nonene	2.16	5,11-Hexadecene	1.32
	3,7-Dimethyl octene	1.71	2,4,6-Trimethyl heptadecene	0.92
	3,3,6-Trimethyl-1,4-heptadiene	5.88	1,19-Eicosadiene	0.76
	3-Ethyl-5-methyl cylcohexane	4.03	4-Eicosene	1.19
	7-Undecene	2.18	1,2,3,5-Tetraisopropyl cyclohexane	1.68
	2-Methyl-Z-4-tetradecene		Unidentified	35.74
Polystyrene	**Aliphatics**		**Aliphatics**	
(PS)	1-Dodecene	0.54	n, $i\text{-}C_{22}$	0.39
	1-Tetradecene	0.65	n, $i\text{-}C_{24}$	0.52
	1-Octadecene	0.94	**Single ring aromatics**	
	1-Nonadecene	0.85	Toluene	0.34
	1-Eicosene	0.43	Styrene	45.11
	2-Methyl tetradecene	0.66	Methyl styrene	0.54
	2,6,10-Trimethyl hexadecene	0.61	Styrene-dimer	12.43
	n, $i\text{-}C_{21}$	0.67	Styrene-trimer	6.23
			Unidentified	29.09

^{a} the doublet chromatographic peaks of α-olefins and n-paraffin were observed

Table 5.4 Major components in pyrolytic oils derived from various materials (cont'd)

Material	Compound	wt.%	Compound	wt.%
Waste tire	**Aliphatics**		**Single ring aromatics**	
(WT)	d-Limonene	12.26	Benzene	1.20
	2-Methyl octane	1.69	Toluene	1.36
	4-Propyl-3-heptene	2.16	Xylene[b]	2.30
	5,8-Diethyl dodecene	1.37	Ethylbenzene	2.81
	2,6,10-Trimethyl dodecene	1.69	**Oxygenates**	
	2-Methyl-Z-4-tetradecene	1.88	Phenol	1.97
	2,6,10-Trimethyl dodecene	7.62	Methyl phenol	1.23
	2,6,10-Trimethyl tetradecene	4.49	2-Hexenyl benzoate	1.92
	C_{21}-C_{28} (Waxes)	17.18	trans-2-undecen-1-ol	1.69
			Unidentified	35.18
Sewage sludge	**Aliphatics**		**Oxygenates**	
(SS)	1-Dodecene	2.16	Methyl phenol	1.19
	n-Dodecane	2.35	Dimethyl phenol	1.04
	1-Tridecene	2.77	1-Decanoic acid	4.52
	n-Tridecane	3.25	1-Dodecanoic acid	3.26
	1-Tetradecene	3.57	Tetradecanoic acid	4.96
	n-Tetradecane	4.02	Hexadecanoic acid	6.29
	Cyclohexadecane	1.22	Octadecanoic acid	10.58
	Single ring aromatics		Cholest-5-en-3-β-ol	1.74
	Benzene	3.63	Steroid	1.22
	Toluene	2.31	**Nitrogenates**	
	Xylene	0.59	Pyrrole	1.85
	Ethylbenzene	0.78	Indole	3.57
	Oxygenates		Methyl indole	4.83
	Phenol	2.24	Trimethyl adenine	3.18
			Unidentified	22.88
Oil sludge	**Aliphatics**		**Aliphatics**	
(OS)	n-C_9[c]	3.82	n-C_{23}	3.12
	n-C_{11}	4.49	n-C_{24}	2.59
	n-C_{12}	5.92	n-C_{25}[c]	2.04
	n-C_{13}	6.22	**Single ring aromatics**	
	n-C_{14}	6.48	Benzene	0.62
	n-C_{15}	6.31	Toluene	2.04
	n-C_{16}	5.71	Xylene[b]	1.22
	n-C_{17}	5.21	Ethylbenzene	0.87
	n-C_{18}	4.94	**Oxygenates**	
	n-C_{19}	4.66	Phenol	0.66
	n-C_{20}	4.49	Methyl phenol	2.77
	n-C_{21}	4.02	Dimethyl phenol	1.75
	n-C_{22}	3.11	Unidentified	16.94

[b] mixed-xylene, o-, m- and p-isomers

[c] the doublet chromatographic peaks of α-olefins and n-paraffin were observed

5.5 Conclusion

Based on a proximate analysis, the materials containing high volatile matters yield high gas and liquid fractions whereas those containing high fixed carbon and ash yield a high solid fraction. However, there are some variations in each fraction which depends on the structure of the materials. The compositions of the derived oils are similar in the content but different in the distribution of products. Four major components can be categories; (*i*) aliphatics (*ii*) single ring aromatics and its alkyl derivatives, (*iii*) oxygenates, and (*iv*) nitrogenates. Each constituent in the derived oil can be speculated from the decomposition of its primer. However, there is no direct relationship between the product composition and its raw material structures.

5.6 Acknowledgements

5.7 References

[1] A.V. Bridgwater, G.V.C. Peacocke, Fast pyrolysis processes for biomass, Renew. Sust. Energ. Rev. 4 (2000) 1-73.

[2] A.V. Bridgwater, Renewable fuels and chemicals by thermal processing of biomass, Chem. Eng. J. 91 (2003) 87-102.

[3] S. Yaman, Pyrolysis of biomass to produce fuels and chemical feedstocks, Energ. Convers. Manage. 45 (2004) 651-671.

[4] T. Malkow, Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal, Waste Manage. 24 (2004) 53-79.

[5] M. Kaltshmitt, D. Thrän, K.R. Smith, Renewable energy from biomass Encyclopedia of physical science and technology, (2002) 203-228.

[6] M.R. Stammbach, B. Kraaz, R. Hagenbucher, W. Richarz, Pyrolysis of sewage sludge in a fluidized bed, Energ. Fuel 3 (1989) 255-259.

[7] M. Inguanzo, A. Domínguez, J.A. Menéndez, C.G. Blanco, J.J. Pis, On the pyrolysis of sewage sludge: The influence of pyrolysis conditions on solid, liquid and gas fractions, J. Anal. Appl. Pyrol. 63 (2002) 209-222.

[8] E. Jakab, M. Omastová, Thermal decomposition of polyolefin/carbon black composites, J. Anal. Appl. Pyrol. 74 (2005) 204-214.

[9] P.T. Williams, E.A. Williams, Interaction of plastics in mixed-plastics pyrolysis, Energ. Fuel 13 (1999) 188-196.

[10] H. Pakdel, D.M. Pantea, C. Roy, Production of dl-limonene by vacuum pyrolysis of used tires, J. Anal. Appl. Pyrol. 57 (2001) 91-107.

[11] C. Amen-Chen, H. Pakdel, C. Roy, Production of monomeric phenols by thermochemical conversion of biomass: A review, Biores. Technol. 79 (2001) 277-299.

[12] T. Karayildirim, J. Yanik, M. Yuksel, H. Bockhorn, Characterisation of products from pyrolysis of waste sludges, Fuel 85 (2006) 1498-1508.

[13] P. Thipkhunthod, V. Meeyoo, P. Rangsunvigit, T. Rirksomboon, Describing sewage sludge pyrolysis kinetics by a combination of biomass fractions decomposition, J. Anal. Appl. Pyrol. 79 (2006) 78-85.

[14] J.M. Encinar, J.F. González, Pyrolysis of synthetic polymers and plastic wastes: Kinetic study, Fuel Process. Technol. 89 (2008) 678-686.

[15] M.R. Islam, H. Haniu, M.R.A. Beg, Liquid fuels and chemicals from pyrolysis of motorcycle tire waste: Product yields, compositions and related properties, Fuel 87 (2007) 3112-3122.

[16] L. Shen, D. Zhang, Low-temperature pyrolysis of sewage sludge and putrescible garbage for fuel oil production, Fuel 84 (2005) 809-815.

[17] H. Schmidt, W. Kaminsky, Pyrolysis of oil sludge in a fluidized bed reactor, Chemosphere 45 (2001) 285-290.

[18] A.M. Cunliffe, P.T. Williams, Compositions of oils derived from the batch pyrolysis of tyres, J. Anal. Appl. Pyrol. 44 (1998) 131-152.

[19] M. Day, D.M. Wiles, Influence of temperature and environment on the thermal decomposition of poly(ethylene terephthalate) fibres with and without the flame retardant tris(2,3-dibromopropyl) phosphate, J Anal. Appl. Pyrol. 7 (1984) 65-82.

[20] J.A. Menéndez, A. Domínguez, M. Inguanzo, J.J. Pis, Microwave pyrolysis of sewage sludge: Analysis of the gas fraction, J. Anal. Appl. Pyrol. 71 (2004) 657-667.

[21] K. Unapumnuk, T.C. Keener, M. Lu, F. Liang, Investigation into the removal of sulfur from tire derived fuel by pyrolysis, Fuel 87 (2008) 951-956.

[22] A. Raave, Organic chemistry of macromolecules-an introductory textbook, Edward Arnold (1967) London.

[23] Y. Liu, J. Quin, J. Wang, Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction, Fuel Process. Technol. 63 (2000) 45-55.

[24] C.-G. Lee, Y.-J. Cho, P.-S. Song, Y. Kang, J.-S. Kim, M.-J. Choi, Effects of temperature distribution on the catalytic pyrolysis of polystyrene waste in a swirling fluidized-bed reactor, Catal. Today 79-80 (2003) 453-464.

[25] S.-S. Kim, S. Kim, Pyrolysis characteristics of polystyrene and polypropylene in a stirred batch reactor, Chem. Eng. J. 98 (2004) 53-60.

[26] M.F. Laresgoiti, B.M. Caballero, I. de Marco, A. Torres, M.A. Cabrero, M.J. Chomón, Characterization of the liquid products obtained in tyre pyrolysis, J. Anal. Appl. Pyrol. 71 (2004) 917-934.

[27] S. Tamura, K. Mukarami, H. Kuwazoe, Isothermal degradation of cis-1,4-polyisoprene vulcanizates, J. Appl. Polym. Sci. 28 (1983) 3467-3484.

[28] S.A. Groves, R.S. Lehrle, M. Blazsó, T. Székely, Natural rubber pyrolysis: Study of temperature- and thickness-dependence indicates dimer formation mechanism, J. Anal. Appl. Pyrol. 19 (1991) 301-309.

[29] D. Van de Meent, J.W. de Leeuw, P.A. Schenck, Origin of unsaturated isoprenoid hydrocarbons in pyrolysates of suspended matter and surface sediments, Phys. Chem. Earth 12 (1980) 469-474.

[30] F. Czechowski, T. Marcinkowski, Sewage sludge stabilization with calcium hydroxide: Effect on physicochemical properties and molecular composition, Water Res. 40 (2006) 1895-1905.

[31] W.C. McCaffery, M.J. Brues, D.G. Cooper, M.R. Kamal, Thermolysis of polyethylene/polystyrene mixtures, J. Anal. Appl. Pyrol. 60 (1996) 2133-2140.