CHAPTER 3

RESULTS AND DISCUSSIONS

3.1. Optimum conditions for extraction of organic components from bio-oil samples

The extraction parameters including organic solvents, extraction modes and extraction times, were optimized in order to get the highest number of the organic components in the extracts. Bio-oil extracts were prepared according to Figure 2.1. The components in these extracts were analyzed by GC-MS. The system of GC-MS instrument is presented in Table 2.1.

3.1.1. Organic solvents

Three organic solvents with different polarity, hexane, dichloromethane and methanol, were used. Before GC-MS analysis, bio-oils were extracted with different organic solvents by ultrasonication for 60 min. The bio-oil was almost completely soluble in hexane. The number of organic compounds of the bio-oils that were extracted using different organic solvents was presented in Figure 3.1.

The result showed that hexane extracts gave the highest number of organic components whereas dichloromethane and methanol extracts gave much lower number of organic components than the first one. This indicated that the components in the bio-oil extracts were mostly non-polar and therefore were not adequately extracted by the more polar solvents. Thus, hexane is the selected solvent for extraction of the bio-oils.

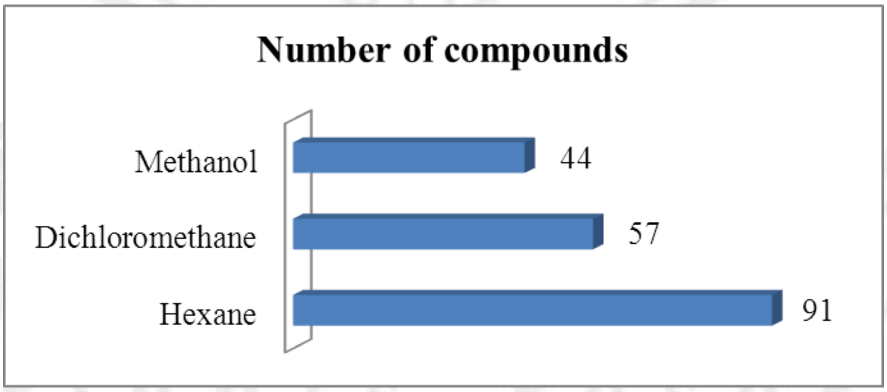

Figure 3.1 The number of organic compounds in bio-oil extracts using different organic solvents obtained by GC-MS

3.1.2. Extraction modes

The extraction modes including ultrasonication and shaking were utilized to extract organic compounds from bio-oils. The bio-oil samples were extracted with hexane by ultrasonication or shaking for 60 min. As shown in Figure 3.2, the number of the organic compounds of the bio-oils obtained from ultrasonication is higher than that obtained from shaking. Thus, ultrasonication was selected as more efficiently technique for extraction of the bio-oil samples.

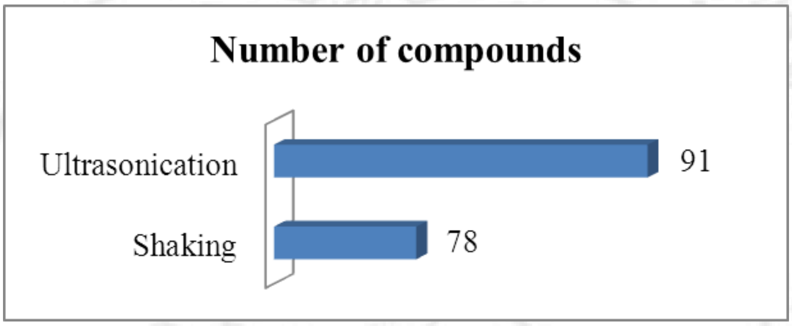

Figure 3.2 The number of organic compounds in bio-oil extracts using different extraction modes obtained by GC-MS

3.1.3. Extraction times

The effect of the extraction time was investigated at 15 min, 30 min and 60 min. The bio-oil samples were extracted with hexane by ultrasonication for 15 min, 30 min or 60 min. It was found that the number of organic compounds obtained at 60 min was higher than the others. The number of organic compounds decreased when the extraction time decreased as shown in Figure 3.3. In addition, the amounts of some compounds in bio-oil extracts obtained at 60 min were higher than these obtained at the other times. Thus, the extraction time 60 min was selected for the extraction condition.

According to the GC-MS analysis, an optimum condition for extraction of organic components from the bio-oil samples was ultrasonication with hexane for 60 min.

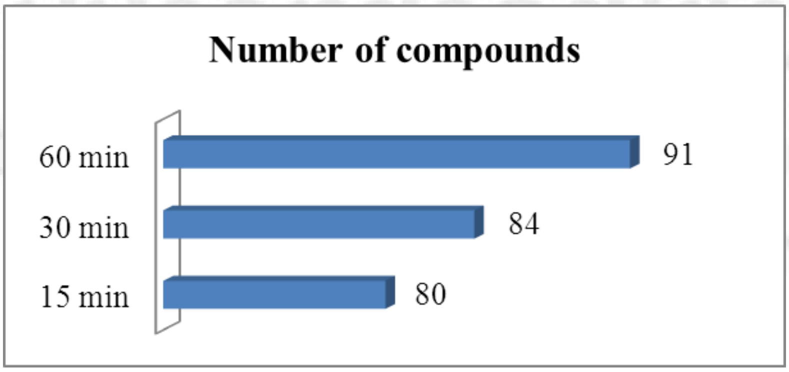

Figure 3.3 The number of organic compounds in bio-oil extracts using different extraction time obtained by GC-MS

3.2. Investigaion of the bio-oil components by gas chromatography-mass spectrometry (GC-MS)

All GC-MS chromatograms of the top and bottom layer of the bio-oil samples obtained from various pyrolysis processes are shown in Figures 3.4-3.7. GC-MS results revealed the detection of 158 and 88 components in the top and bottom layer samples, respectively. Among these, there were 83 and 50 components, respectively, identified based on the mass spectrum matching against those compiled in the mass spectral library (NIST08 Mass Spectral Library, National Institute of Standards and Technology, USA).The obvious complexity of the samples was clearly visible, so that GCxGC-TOF-MS was chosen as a more efficient technique for further separation of the bio-oil samples.

Figures 3.4-3.5, show organic components of the top layer bio-oil obtained using pyrolysis temperatures 400 °C, 500 °C and 600 °C at heating rate of 10 °C/min and 50 °C/min. The result showed that the pyrolysis process using temperature of 400 °C and heating rate of 10 °C/min gave the highest number of organic components than the other temperatures, same as using heating rates of 50 °C/min. In addition, the pyrolysis process using temperature 400 °C and heating rate 10 °C/min gave the highest number of organic components in the top layer bio-oils.

From GC-MS analysis, 158 components were detected and 83 components were tentatively identified in these oils. The chromatograms showed very complicated, so about 47 % of all organic compounds could not identified. The major compounds were phenol, 2-methylphenol, 4-methylphenol, 4-ethylphenol, caffeine and 3,7,11,15-tetramethyl-2-hexadecen-1-ol. The major groups of these bio-oil samples were phenolics, hydrocarbons and N-heterocyclic derivatives. The % relative contents of phenolics, hydrocarbons and N-heterocyclic derivatives of all bio-oil samples were about 39%, 18%, and 11%, respectively.

It was also found that the phenolics content increased as the pyrolysis temperature increased from 400 °C to 600 °C. On the other hand, the hydrocarbons content decreased when increasing the temperature. The same results were obtained in both heating rates.

GC-MS chromatograms of the bottom layer bio-oils obtained by various pyrolysis processes are shown in Figures 3.6-3.7. The results obtained from GC-MS showed that the pyrolysis process using temperature 400 °C and heating rate 10 °C/min gave the highest number of organic components in the bottom layer bio-oils as same as the top layer bio-oils. It revealed the detection of 88 components in bio-oils. Among these, there were 50 components identified. It can be clearly seen that the organic components in the bottom layer were lower than in the top layer of bio-oils. Especially in the hydrocarbons, they were not found in the bottom layer of the bio-oil because bottom layer is water phase therefore hydrocarbons, non-polar compounds, were not soluble in this layer. However, some phenolics, including phenol, 4-methylphenol, 2-methoxy phenol, 4-methylphenol were found as the major products of the bio-oils same as the top layer bio-oils. Besides phenolics, N-heterocyclic derivatives such as caffeine were the major products too. The contents of phenolics were found in the bottom layer higher than in the top layer, as well as N-heterocyclic derivatives.

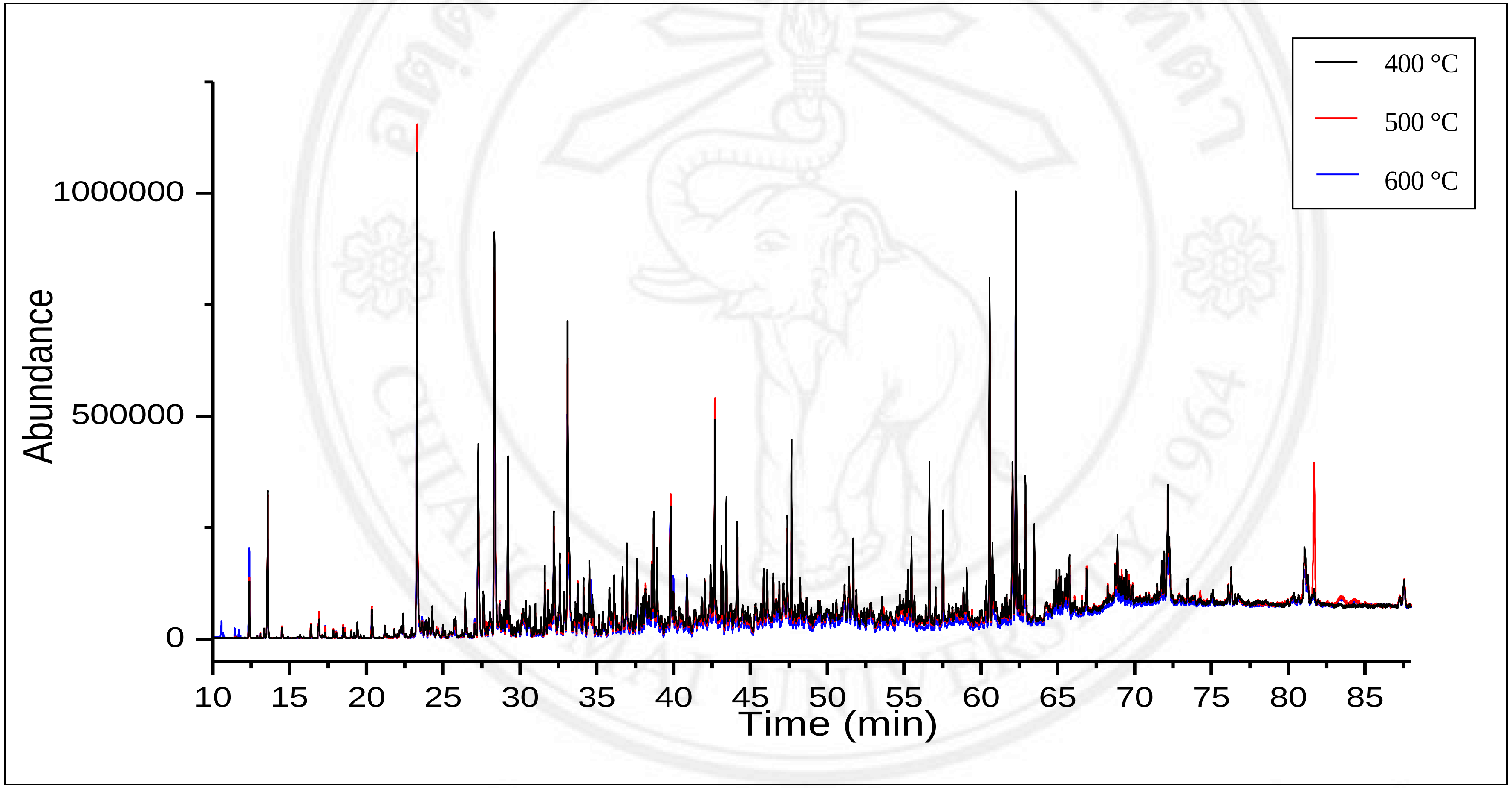

Figure 3.4 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperatures of 400 °C, 500 °C and 600 °C at heating rate of 10 °C/min

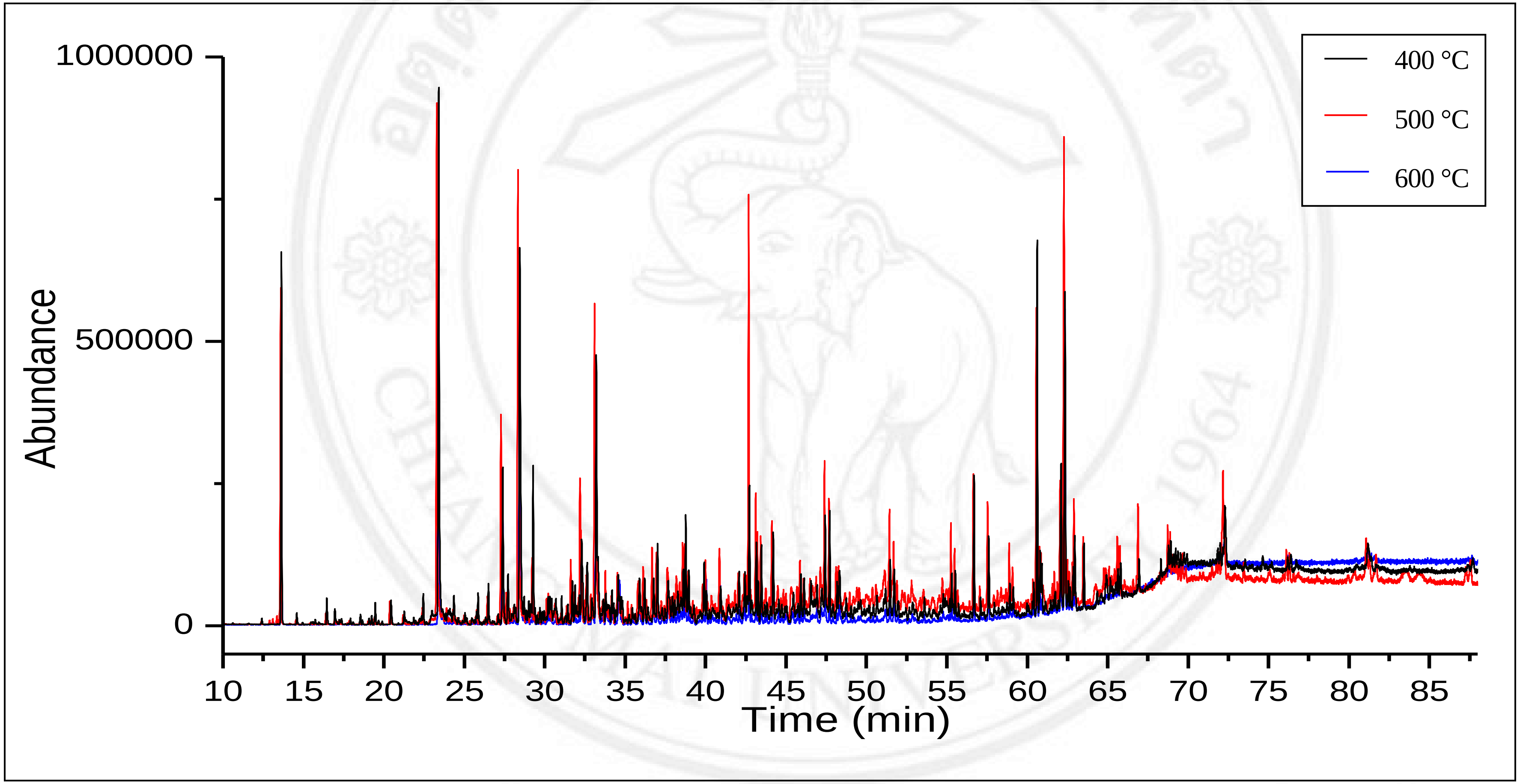

Figure 3.5 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperatures of 400 °C, 500 °C and 600 °C at heating rate of 50 °C/min

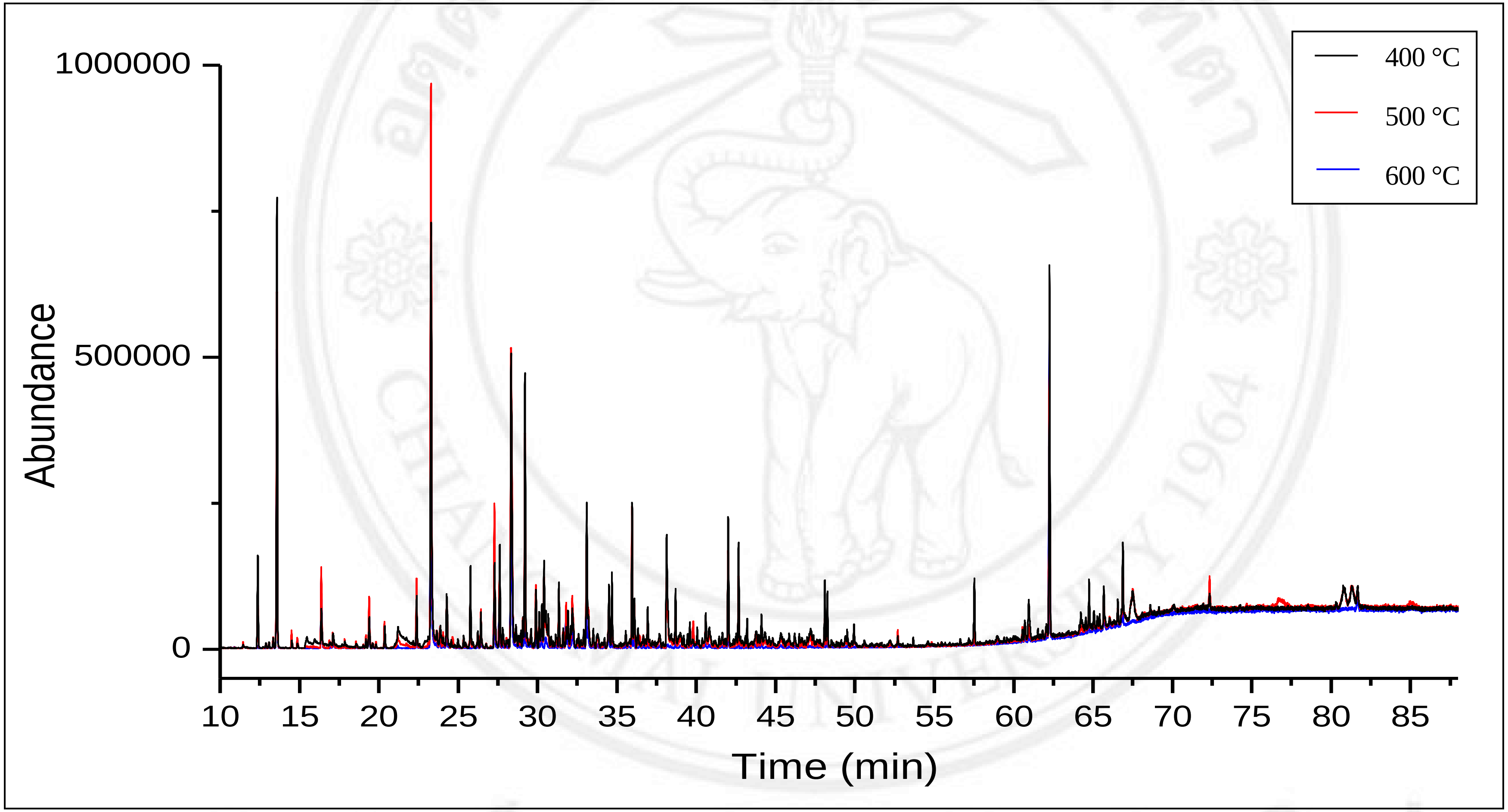

Figure 3.6 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperatures of 400 °C, 500 °C and 600 °C at heating rate vof 10 °C/min

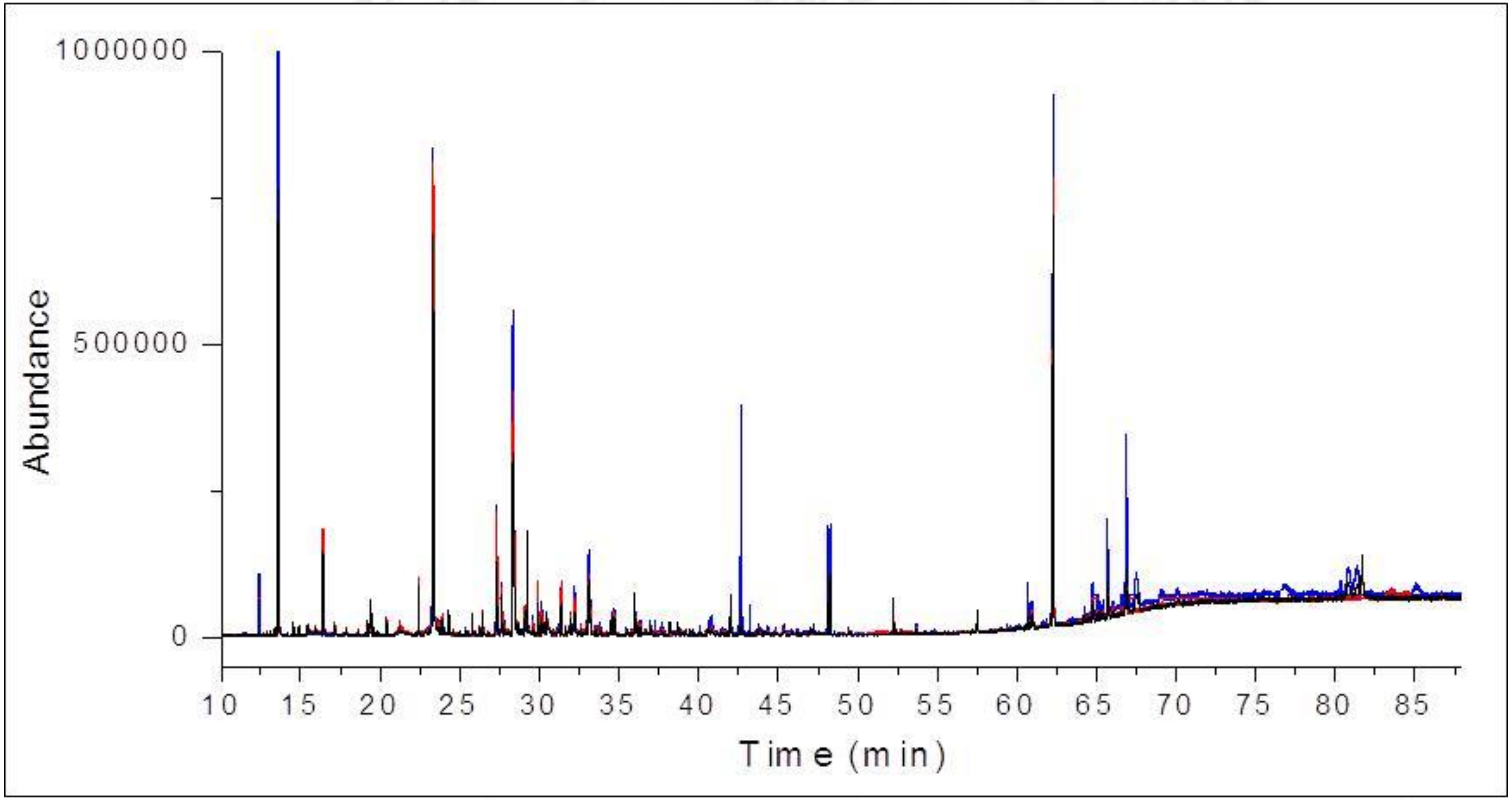

Figure 3.7 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperatures of 400 °C, 500 °C and 600 °C at heating rate of 50 °C/min

3.3. Identification of the bio-oil components by comprehensive two-dimensional gas chromatography (GC×GC)

From Figures 3.4-3.7, the complexity of the samples was clearly visible, so that GCxGC-TOF-MS was chosen as a more efficient technique for further separation of the bio-oil samples.

GC×GC technique was applied to the analysis of the organic components in the tea waste bio-oil samples in order to increase chromatographic resolution. The2D and 3D plot of the visualization featuresof the mixed bio-oil sample which was analyzed by GC×GC-TOF-MS is depicted in Figure 3.8. Group type classification of the bio-oil components is demonstrated in Figure 3.9.The series of hydrocarbons were clearly visiblein the 2D and 3D surface plots.

The bio-oil components were classified by chemical functional groups on the 2D contour plot as shown in Figure 3.9. The components are ordered by boiling point on the first column (Rtx-5MS) and increasing polarity on the second column (Rti-5Sil MS). This resulted in 5 groups, hydrocarbons, phenolics, aromatic compounds, alcohols and *N*- and *O*-heterocyclic aromatic derivatives. The aromatics can be subdivided into mono- and di-aromatics such as alkyl benzenes and naphthalenes. The heterocyclic aromatic compounds consisted mostly of *N*-heterocyclic derivatives containing compounds like pyridines and pyrazines.

All individual bio-oil samples were analyzed by GC×GC-FID and identification was performed by comparing with the 2D plot of the mixed bio-oil sample.The GC×GC contour plots of the top and bottom layer of the bio-oils are shown in Figures 3.10-3.21.The identified components of both layersare shown in Figures 3.22–3.27 and Figures 3.29-3.34. Their relative peak area percents are illustrated Tables 3.1 and 3.2. The “unknown” compounds consisted of compounds with lowsimilarity or false matching hits with the mass spectral library of ChromaToF software.

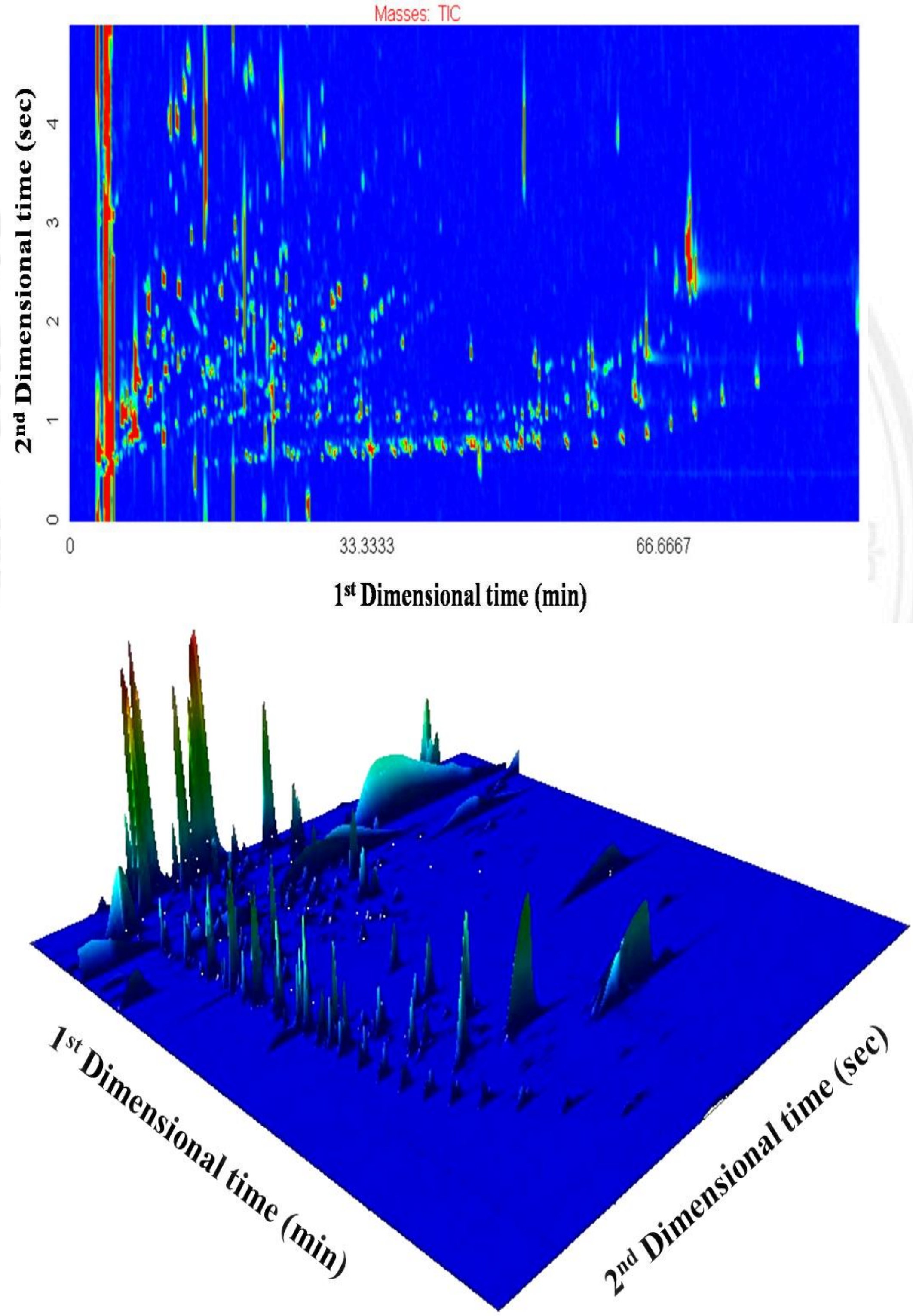

Figure 3.8 2D and 3D surface plots of the mixed bio-oil sample

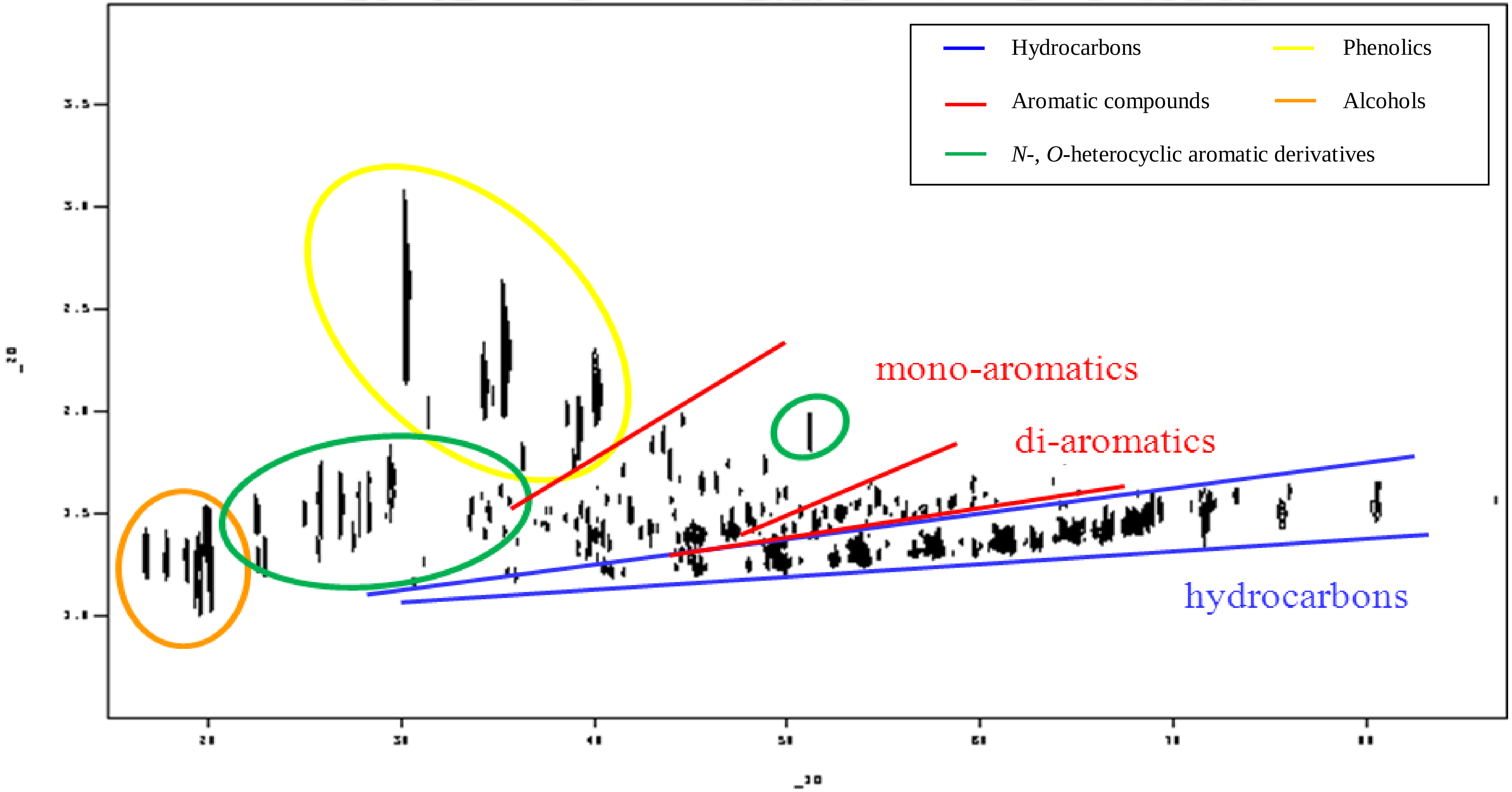

Figure 3.9 Group type classification of the components in tea waste bio-oil obtained from top layer with pyrolysis temperature of 600 °C and heating rate of 50 °C/min

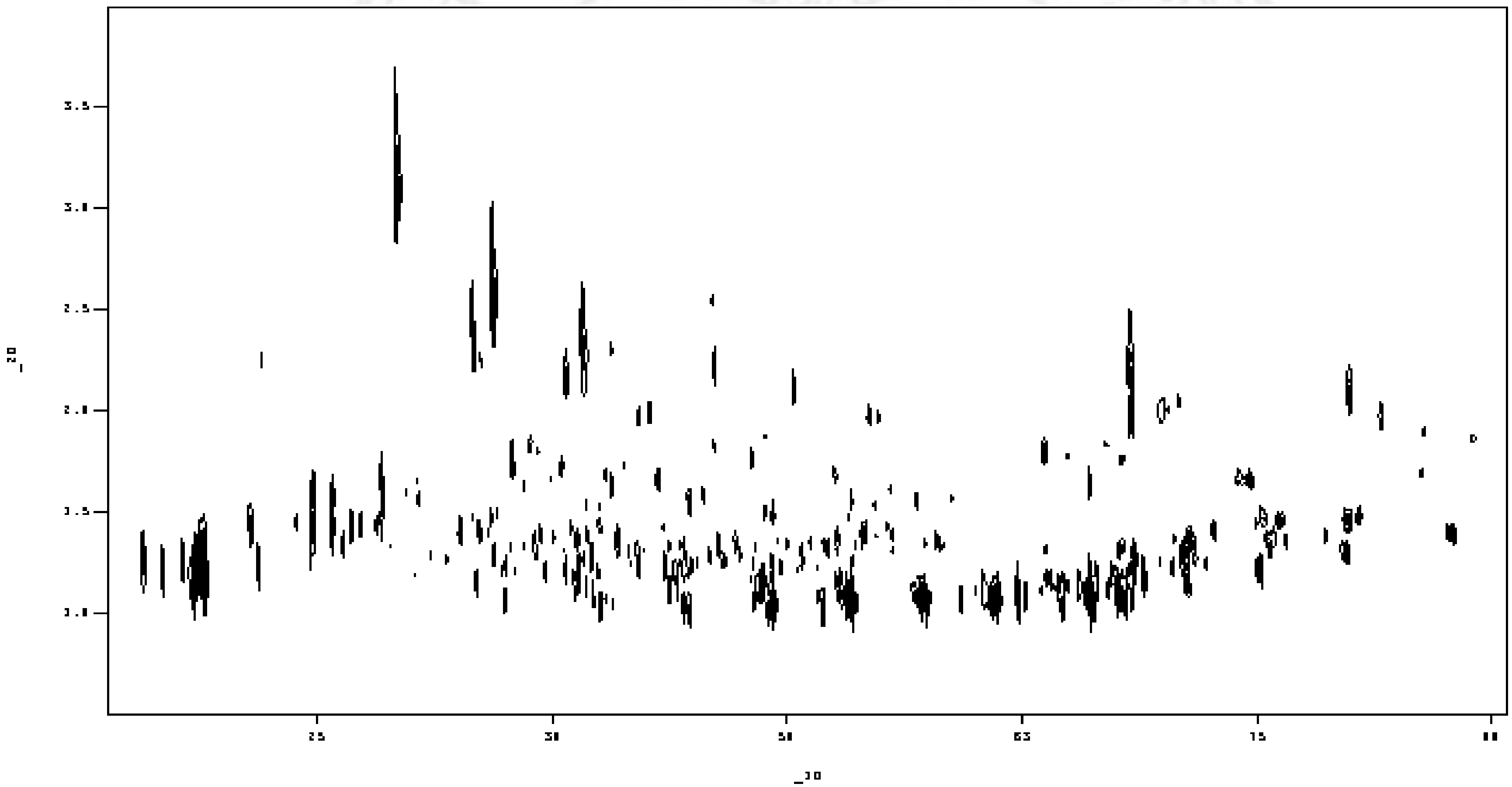

Figure 3.10 GC×GC contour plot of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min

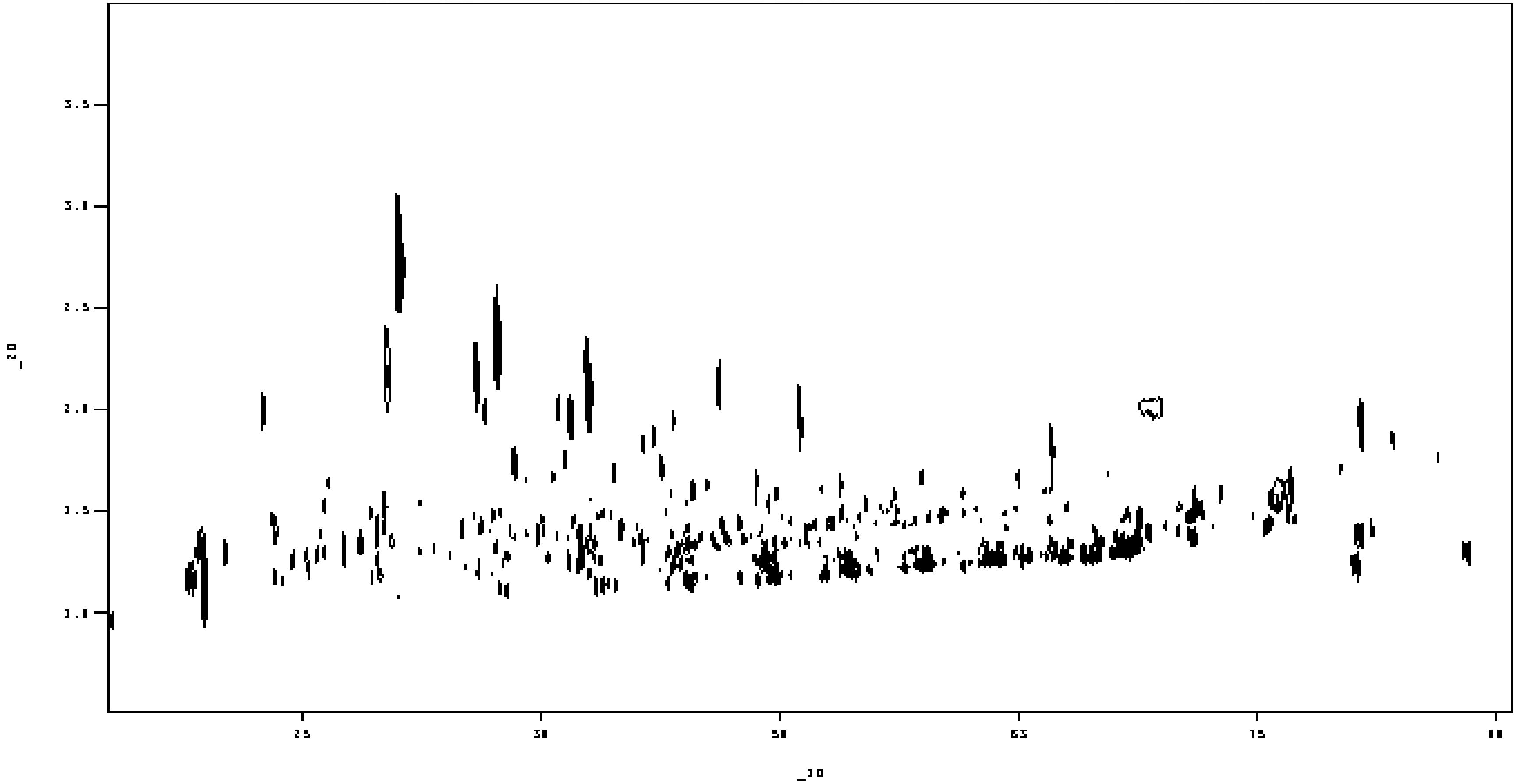

Figure 3.11 GC×GC contour plot of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min

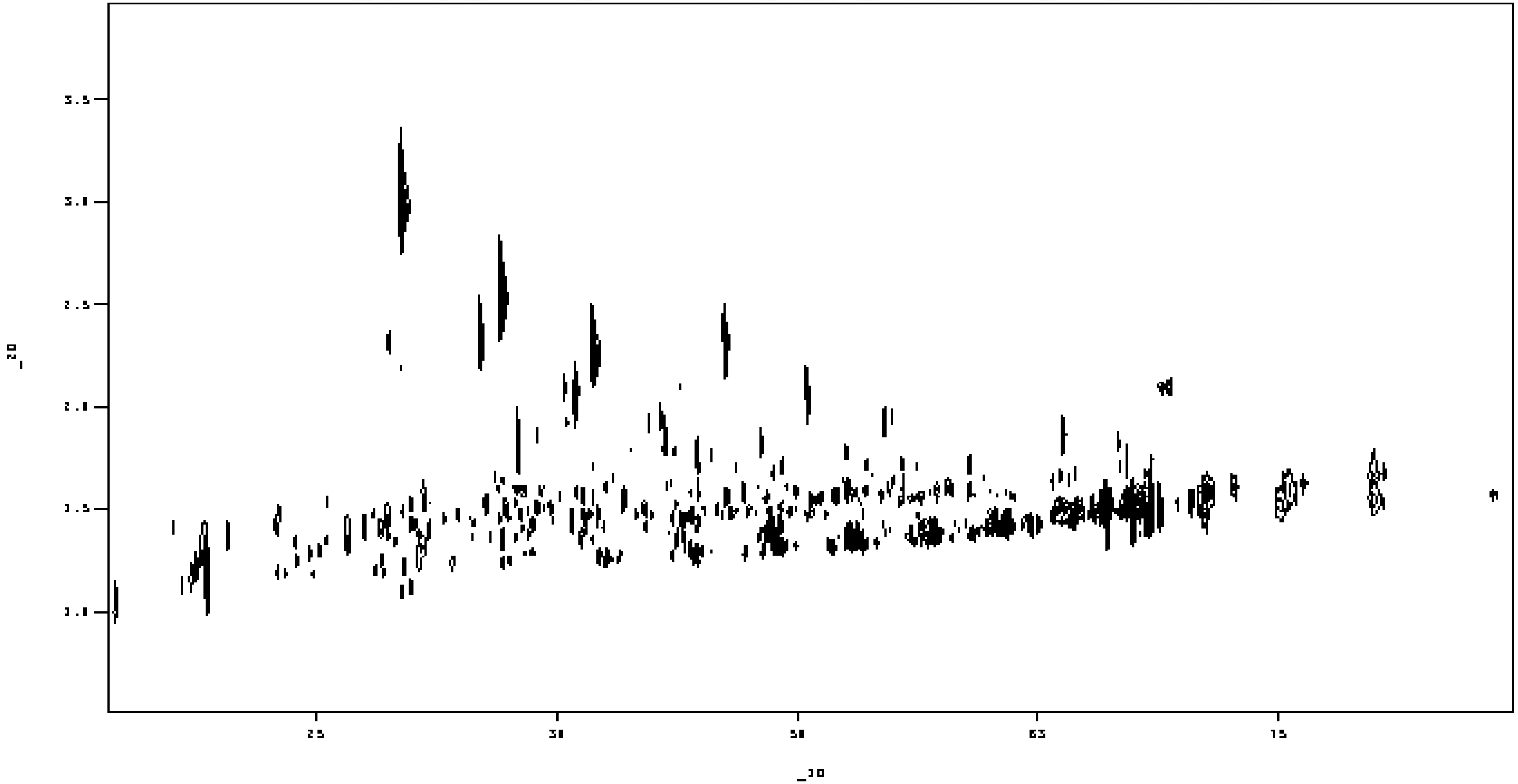

Figure 3.12 GC×GC contour plot of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min

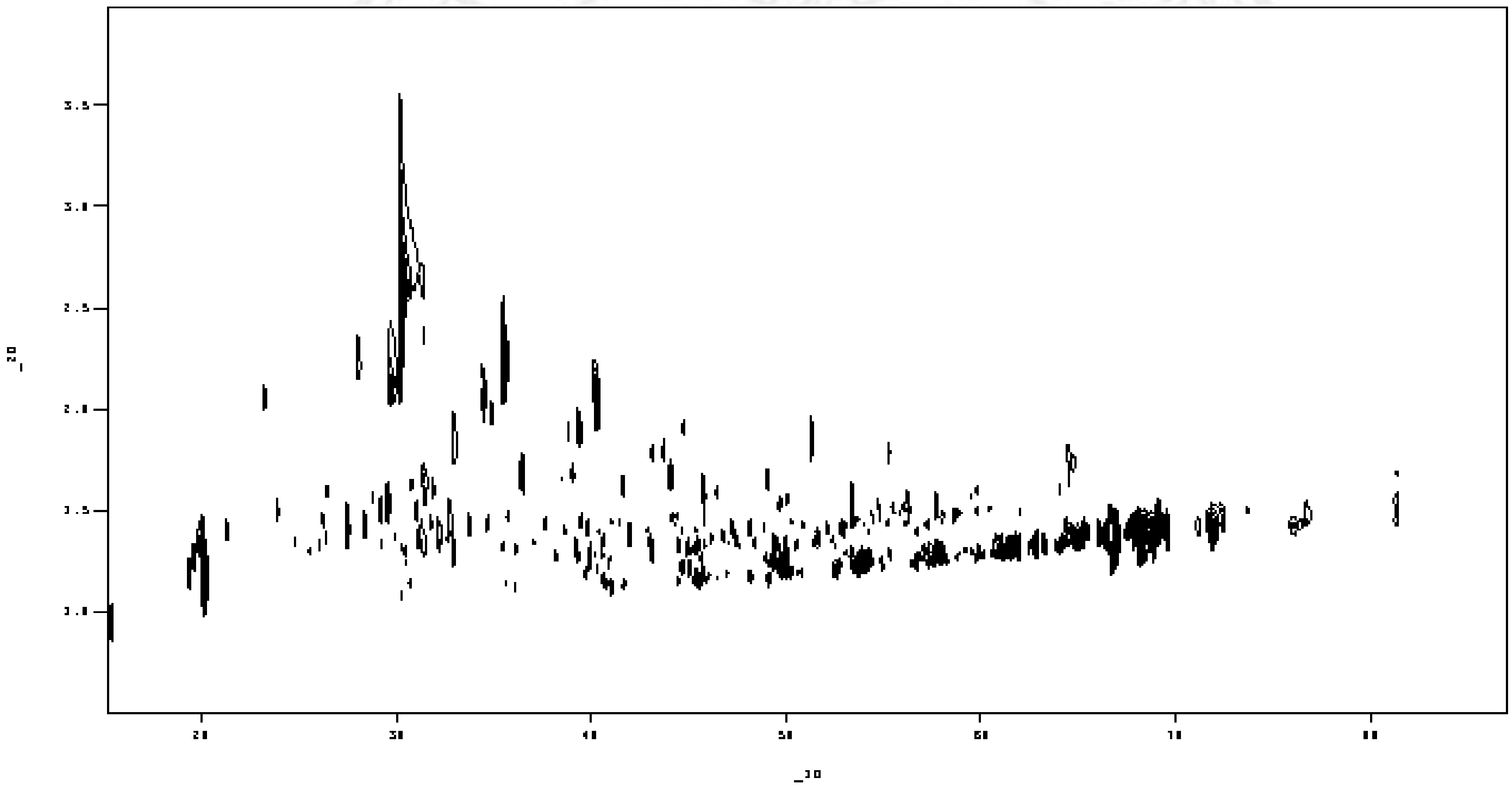

Figure 3.13 GC×GC contour plot of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min

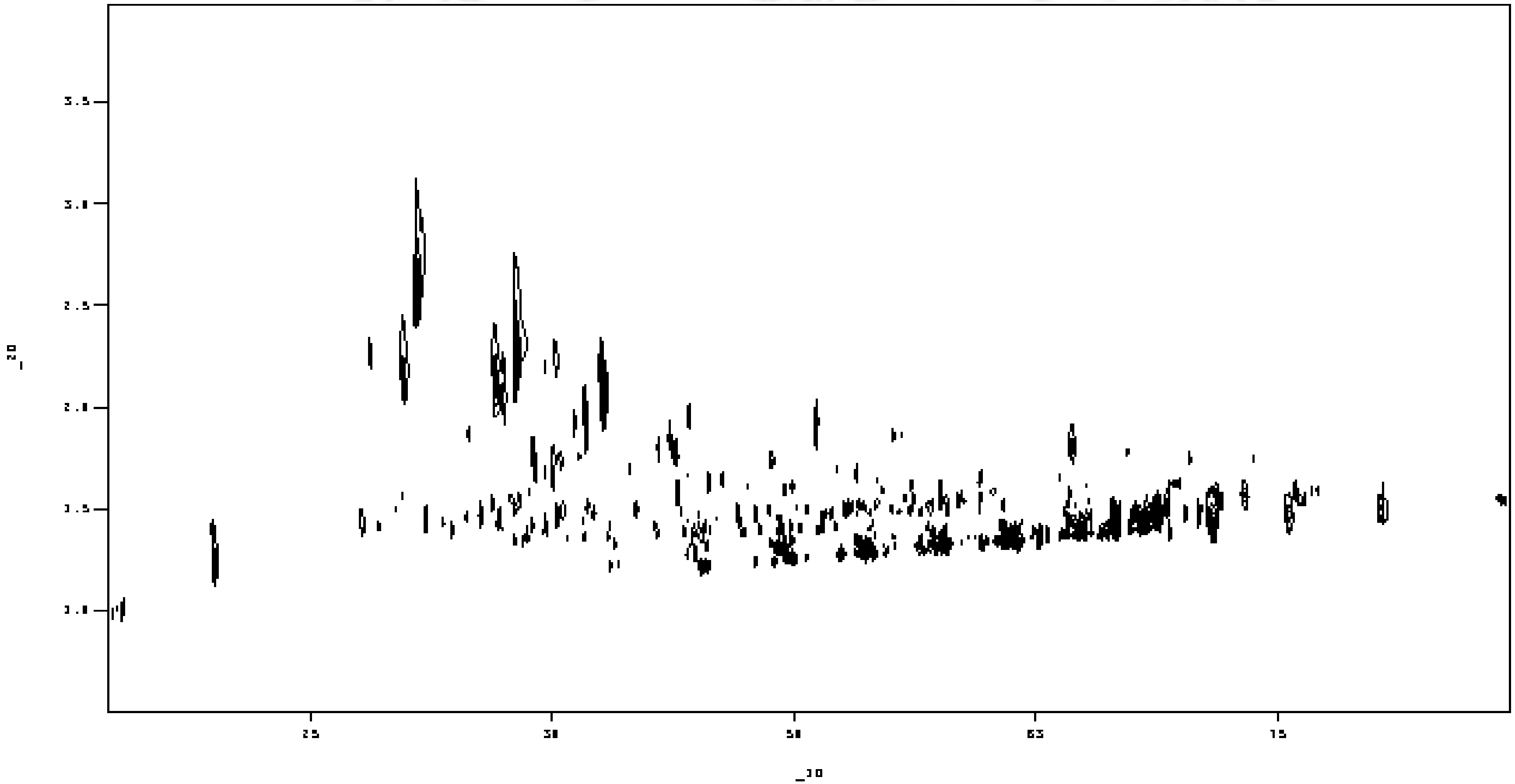

Figure 3.14 GC×GC contour plot of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min

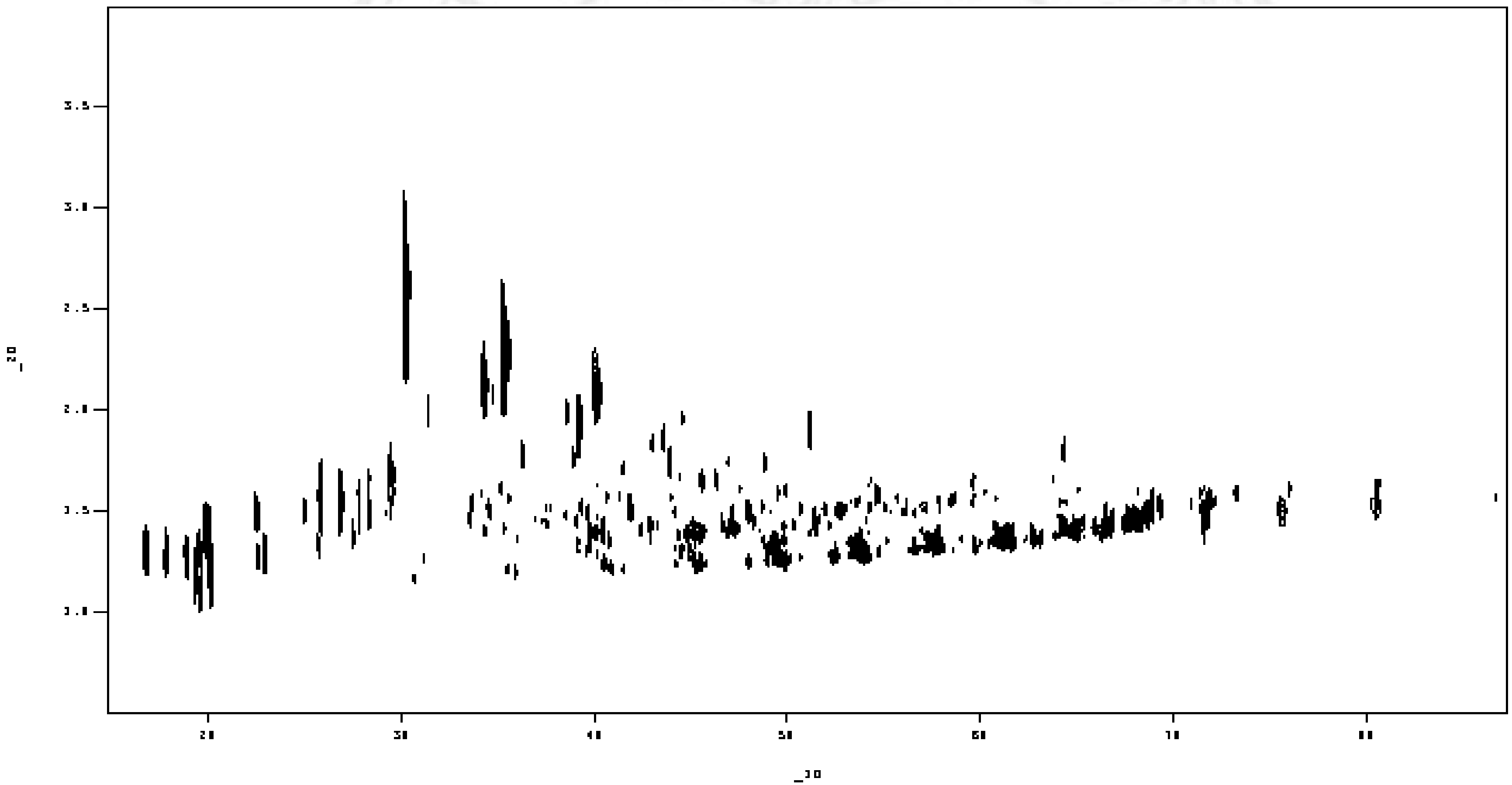

Figure 3.15 GC×GC contour plot of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min

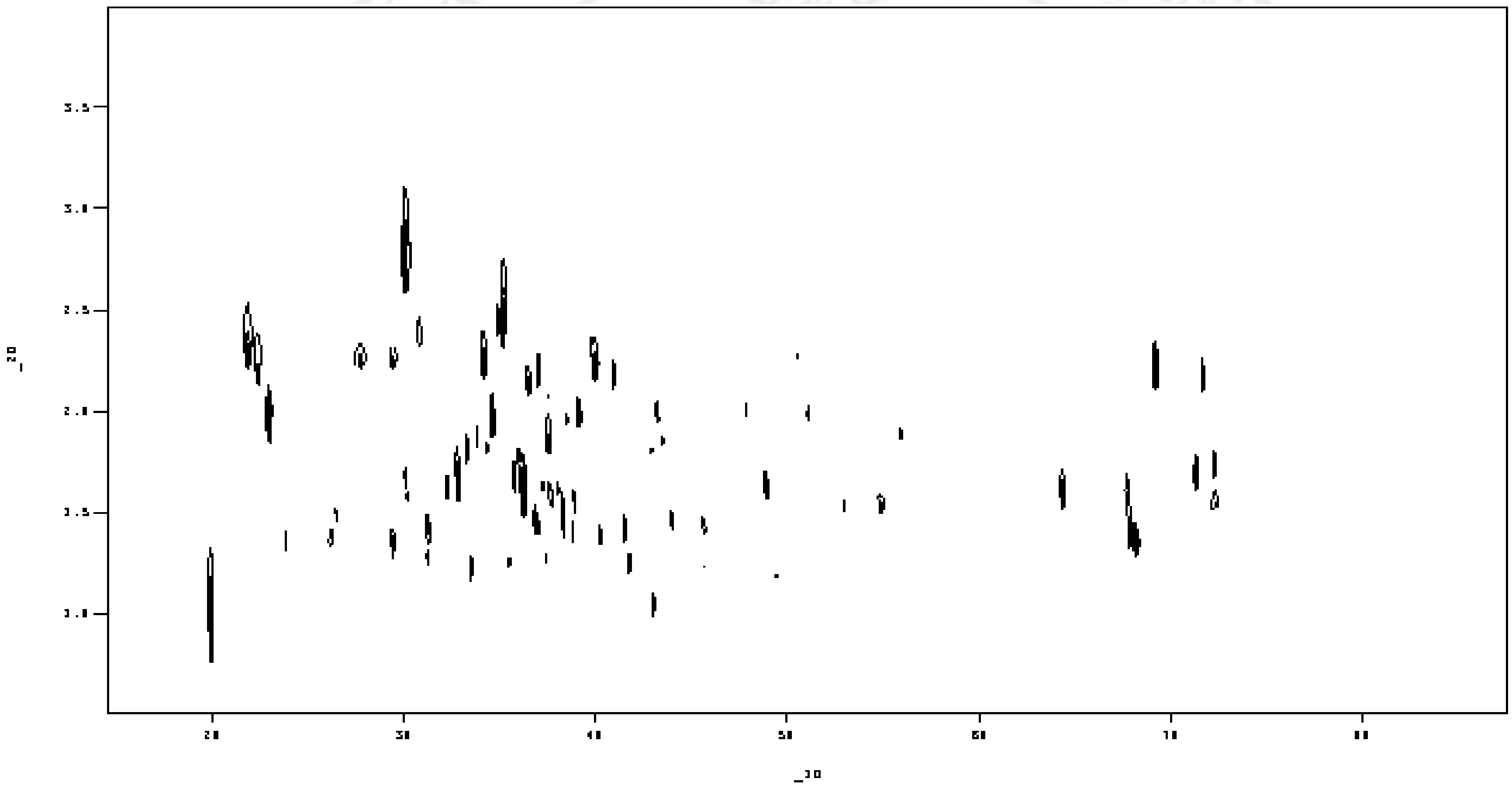

Figure 3.16 GC×GC contour plot of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min

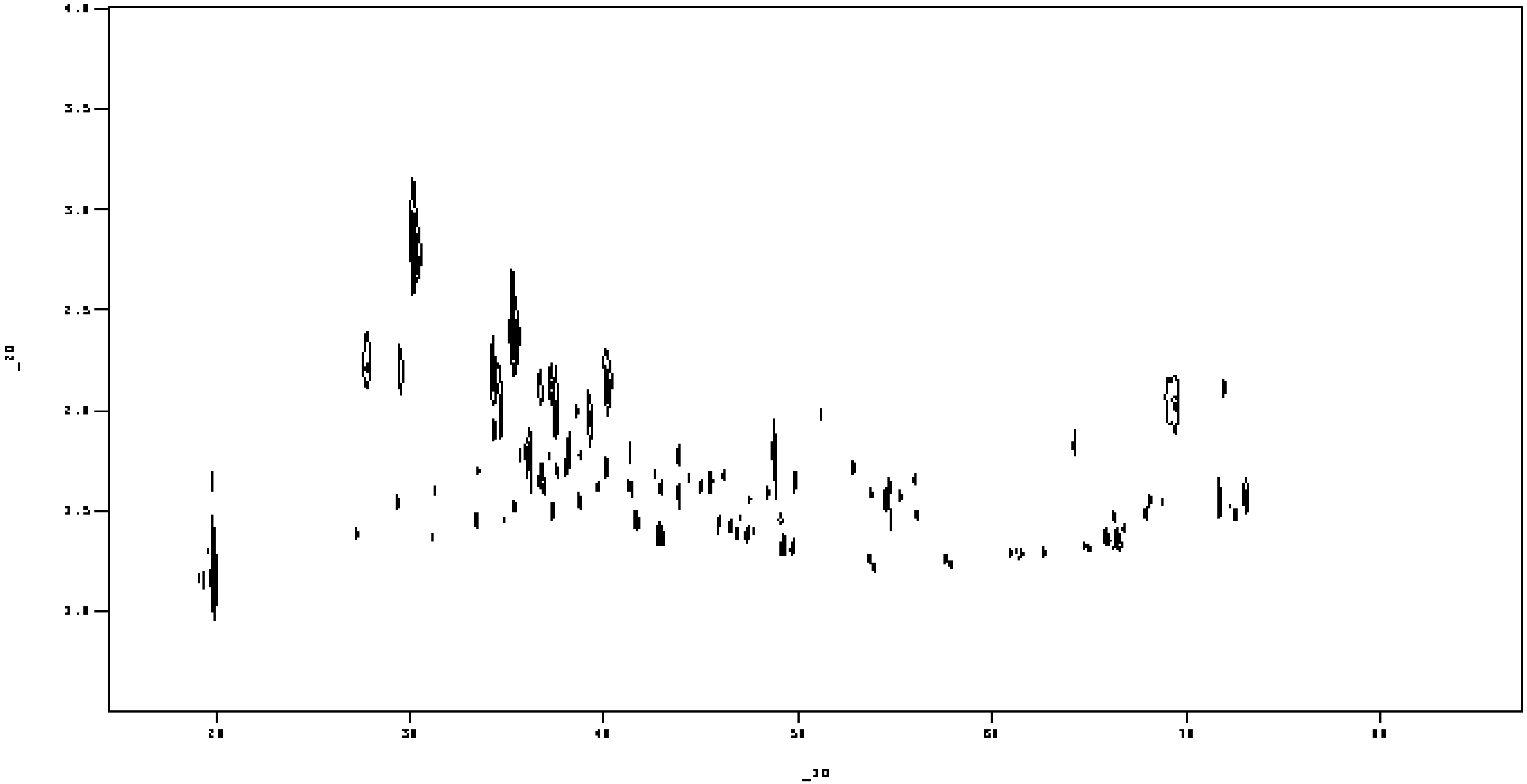

Figure 3.17 GC×GC contour plot of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min

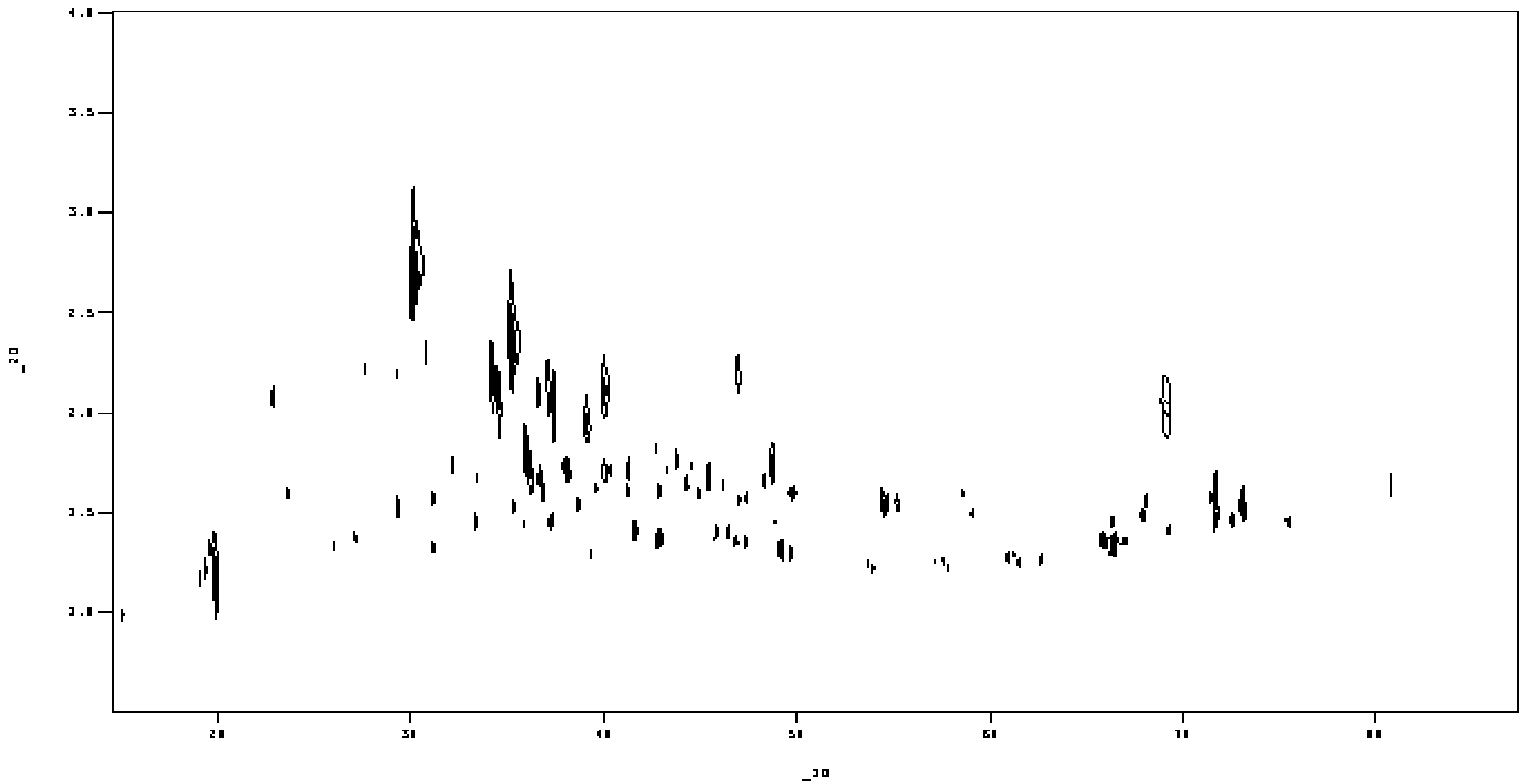

Figure 3.18 GC×GC contour plot of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min

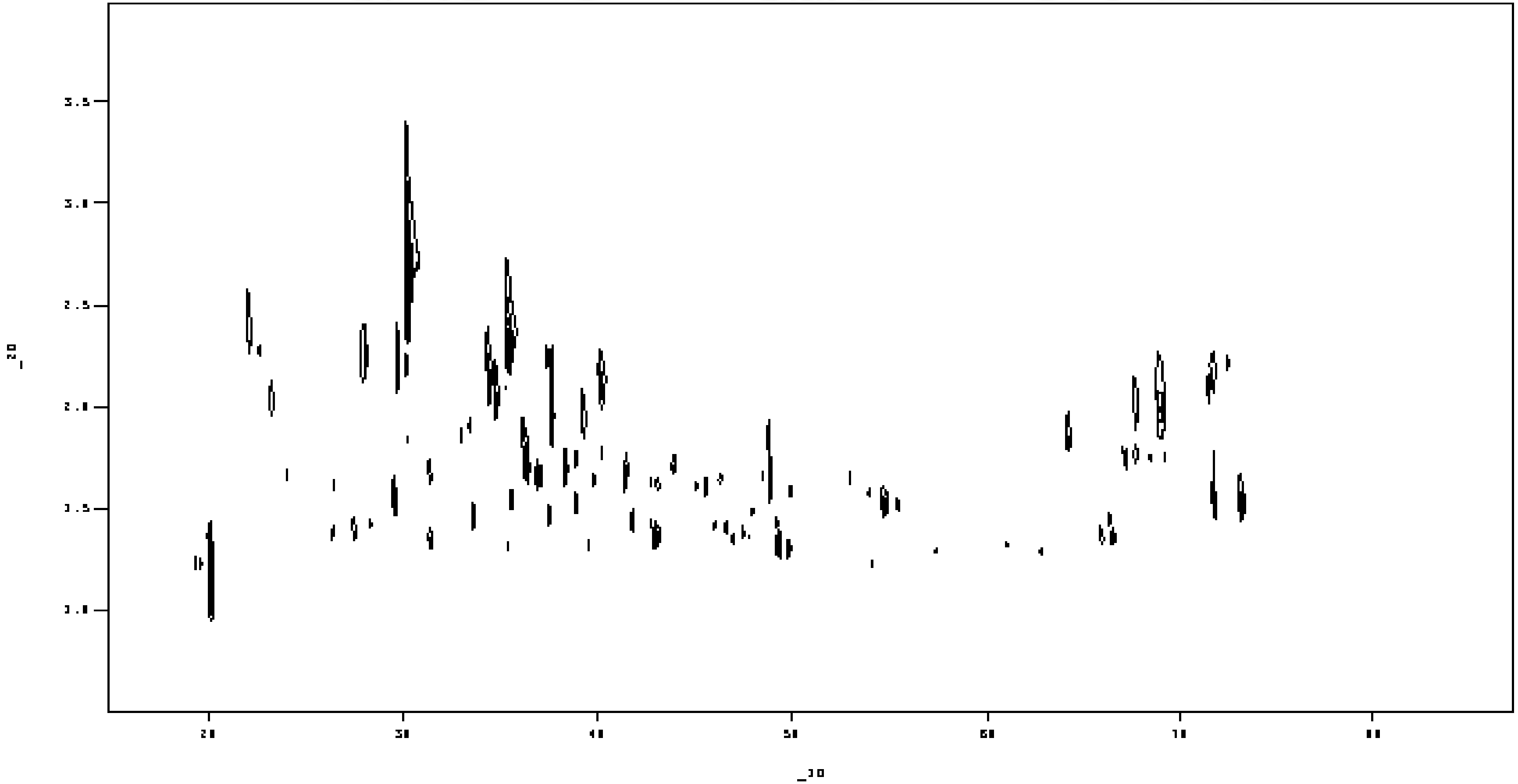

Figure 3.19 GC×GC contour plot of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min

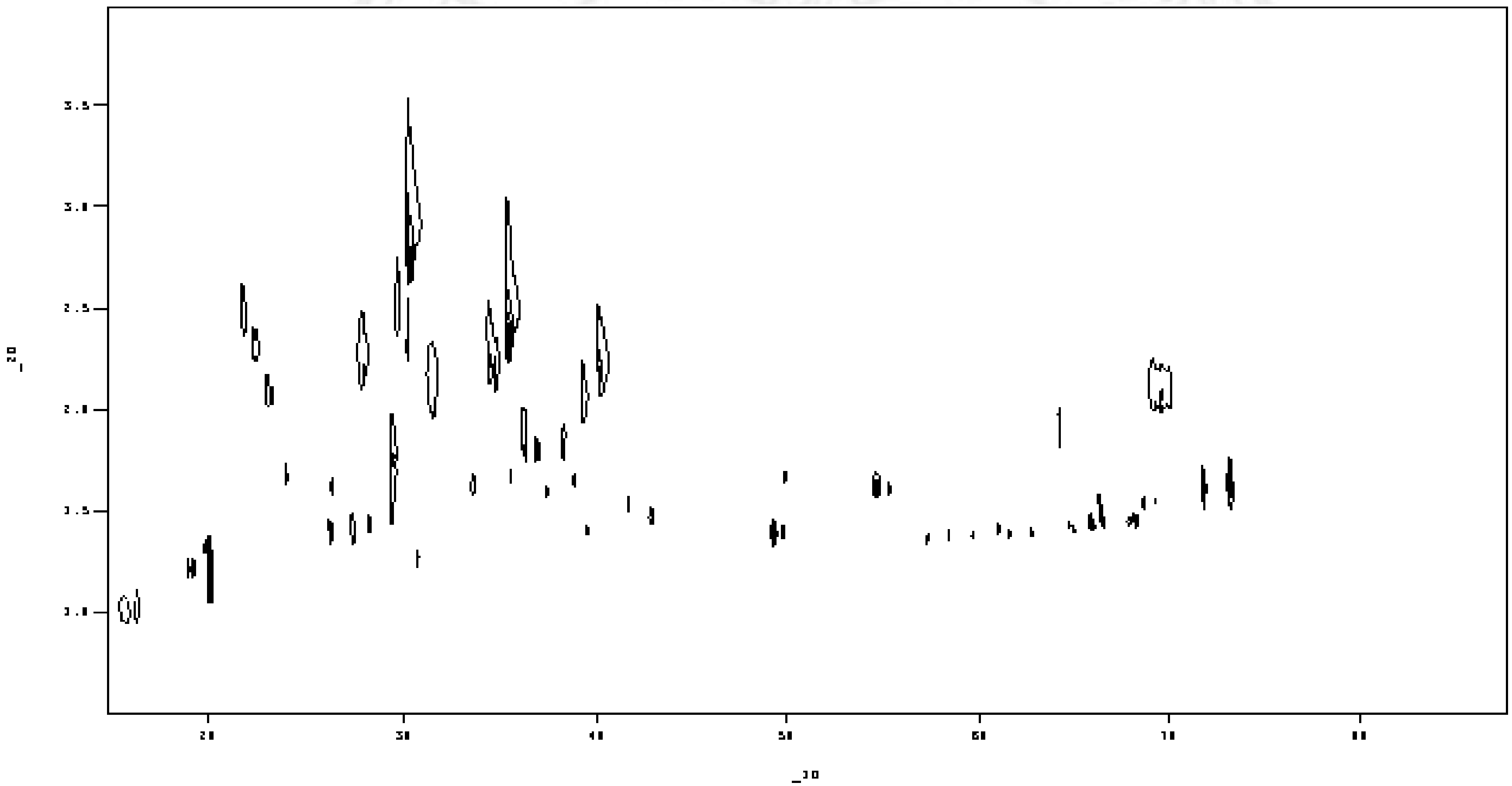

Figure 3.20 GC×GC contour plot of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min

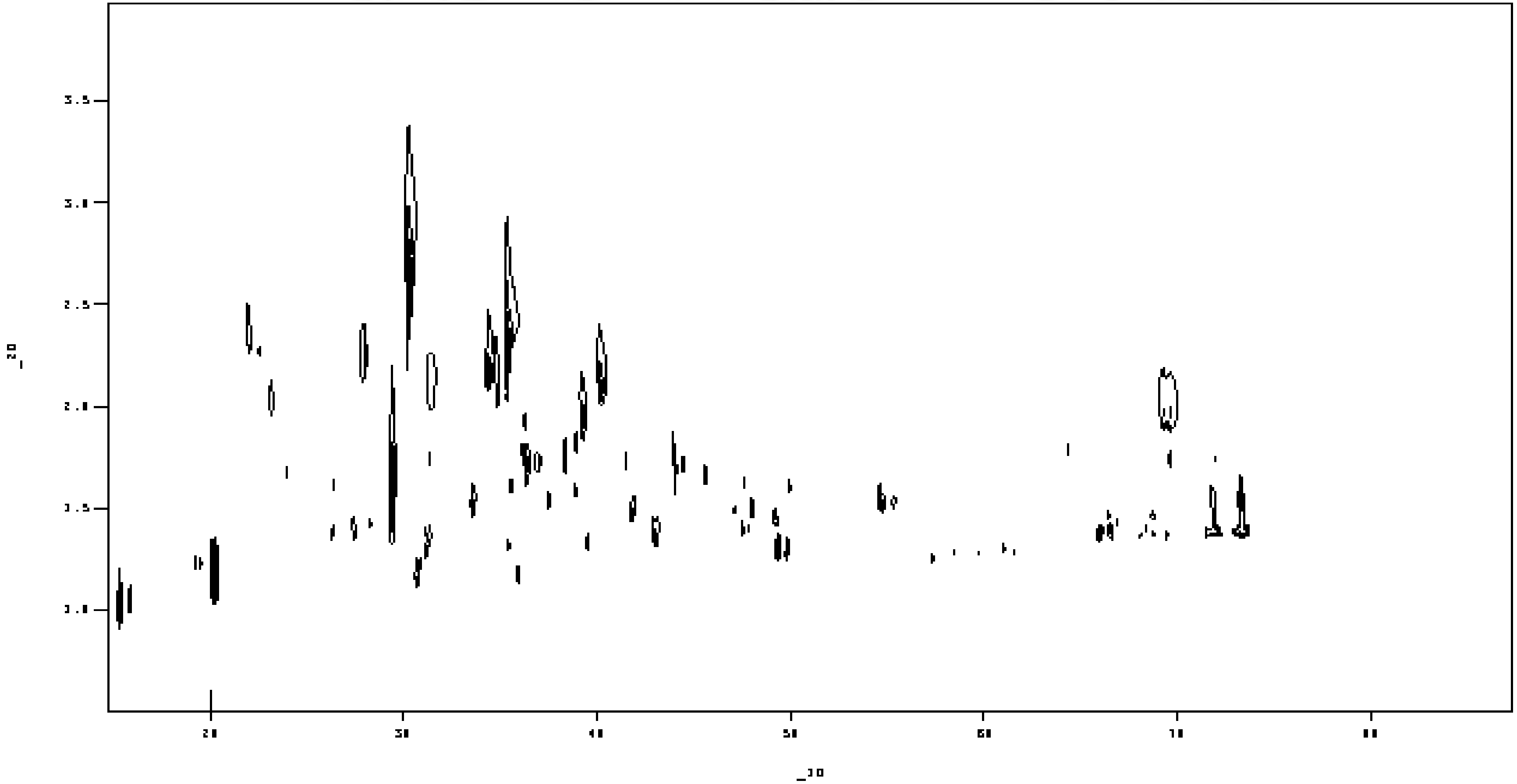

Figure 3.21 GC×GC contour plot of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min

GC×GC contour plots of the top layer bio-oil are shown in Figures 3.10–3.15. The identified components of the top layer bio-oils are presented in Figures 3.22–3.27 and listed in Table 3.1. The contour plots showed the series of hydrocarbons as group classified in Figure 3.9. From the contour plots, hydrocarbons presented at low level of 2^{nd} dimensional time (y axis) because they are low polarity compounds. On the other hand, phenolics which have higher polarity presented at upper level than hydrocarbons. The large and dark spot indicated that the amounts of these phenolics were very high.

GC×GC contour plots of the bottom layer bio-oils are presented in Figures 3.16–3.21 and the identified compounds are shown in Figures 3.29–3.34 and listed in Table 3.2. All contour plots show slight number of organic components, not as complicated as the top layer. The series of hydrocarbons were not found in the contour plots because the bottom layer is aqueous phase.

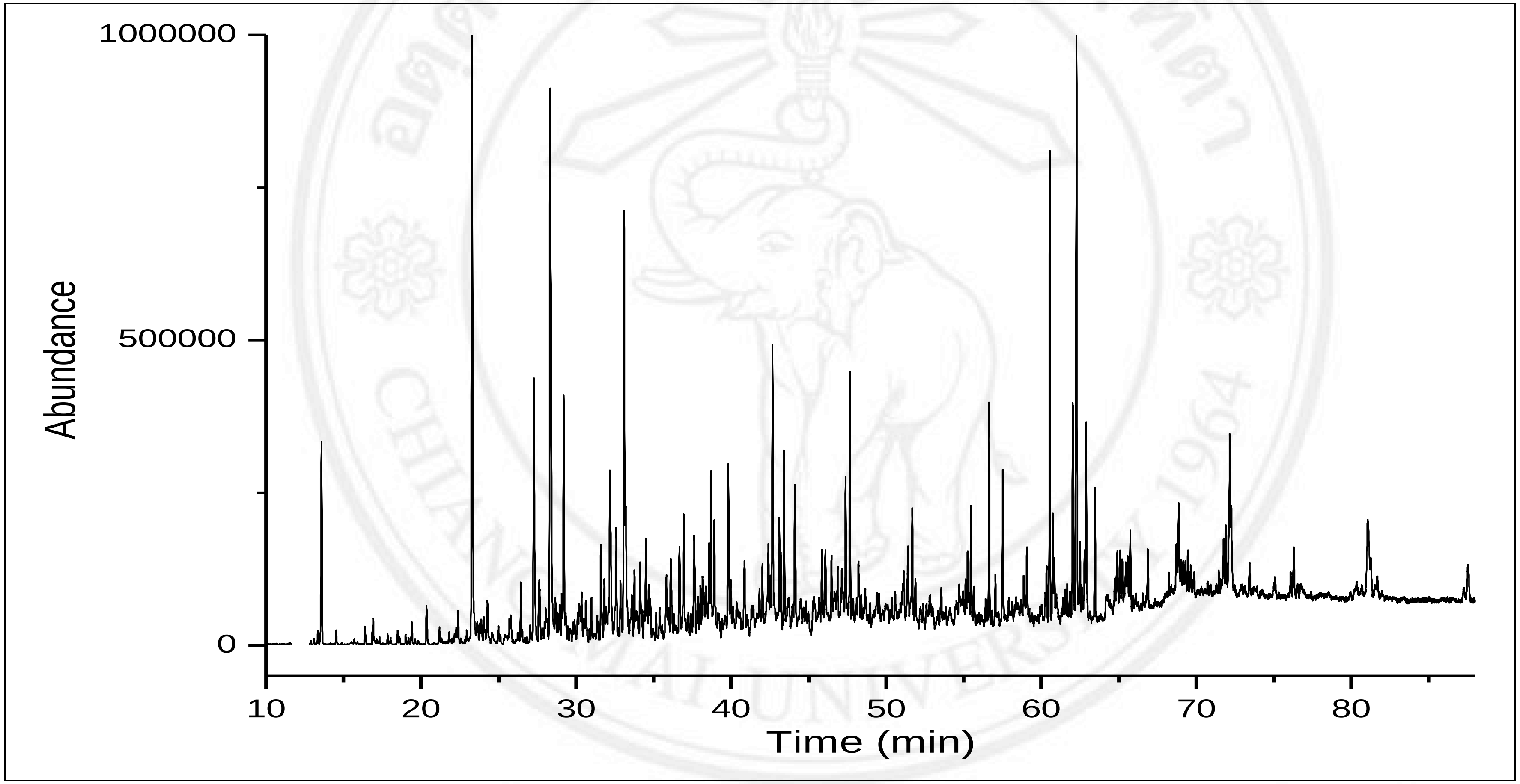

Figure 3.22 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min

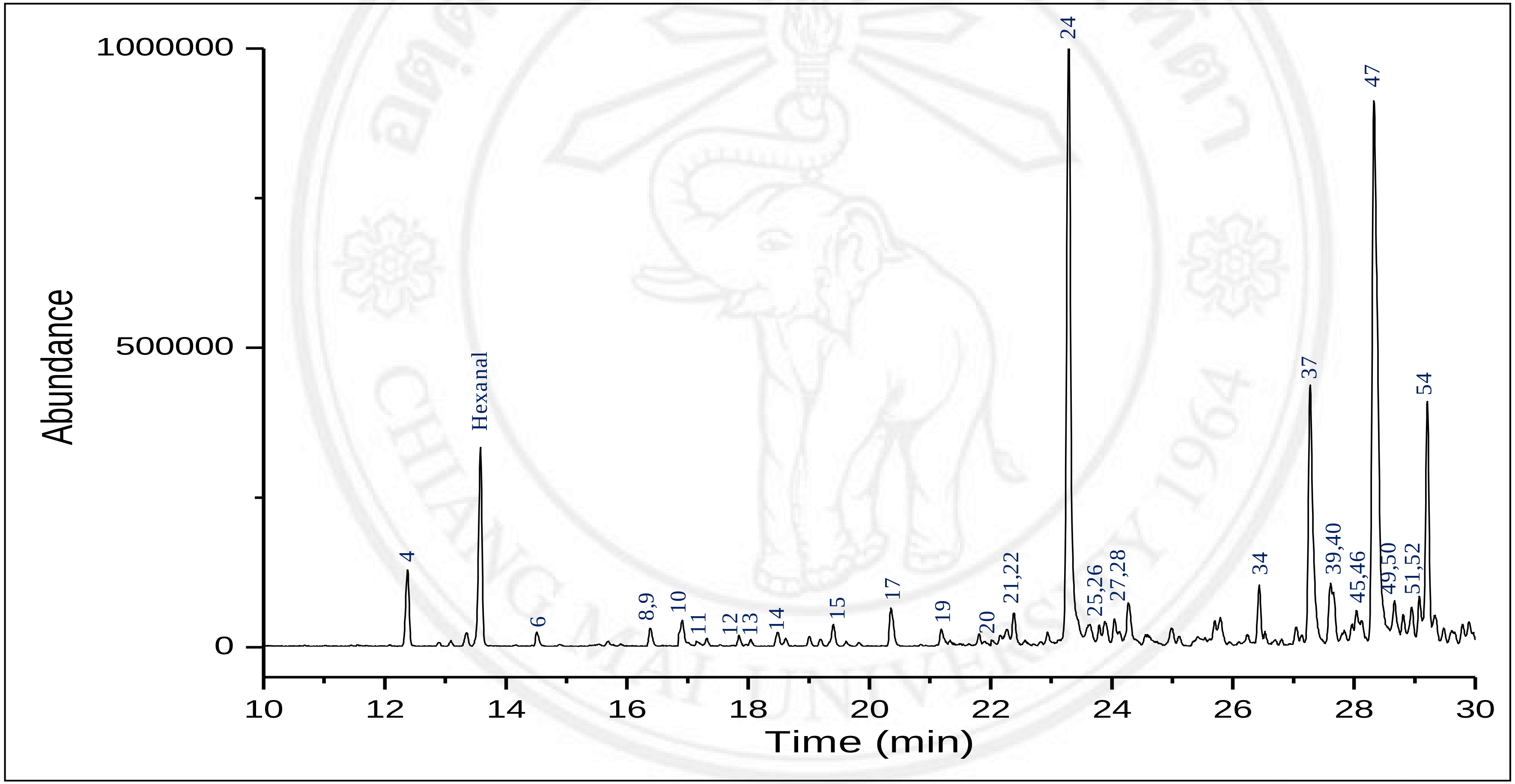

Figure 3.22 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued)

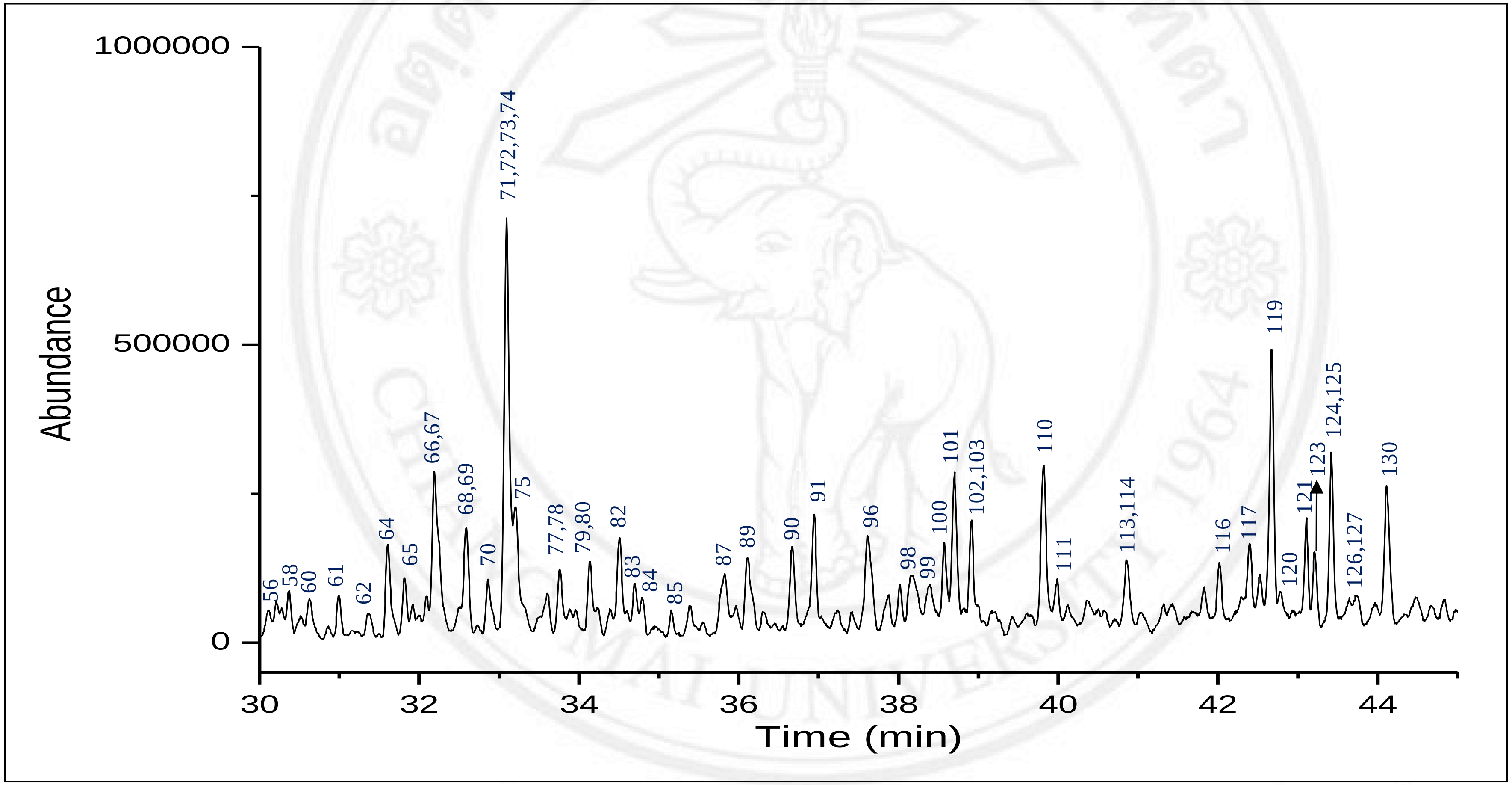

Figure 3.22 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued)

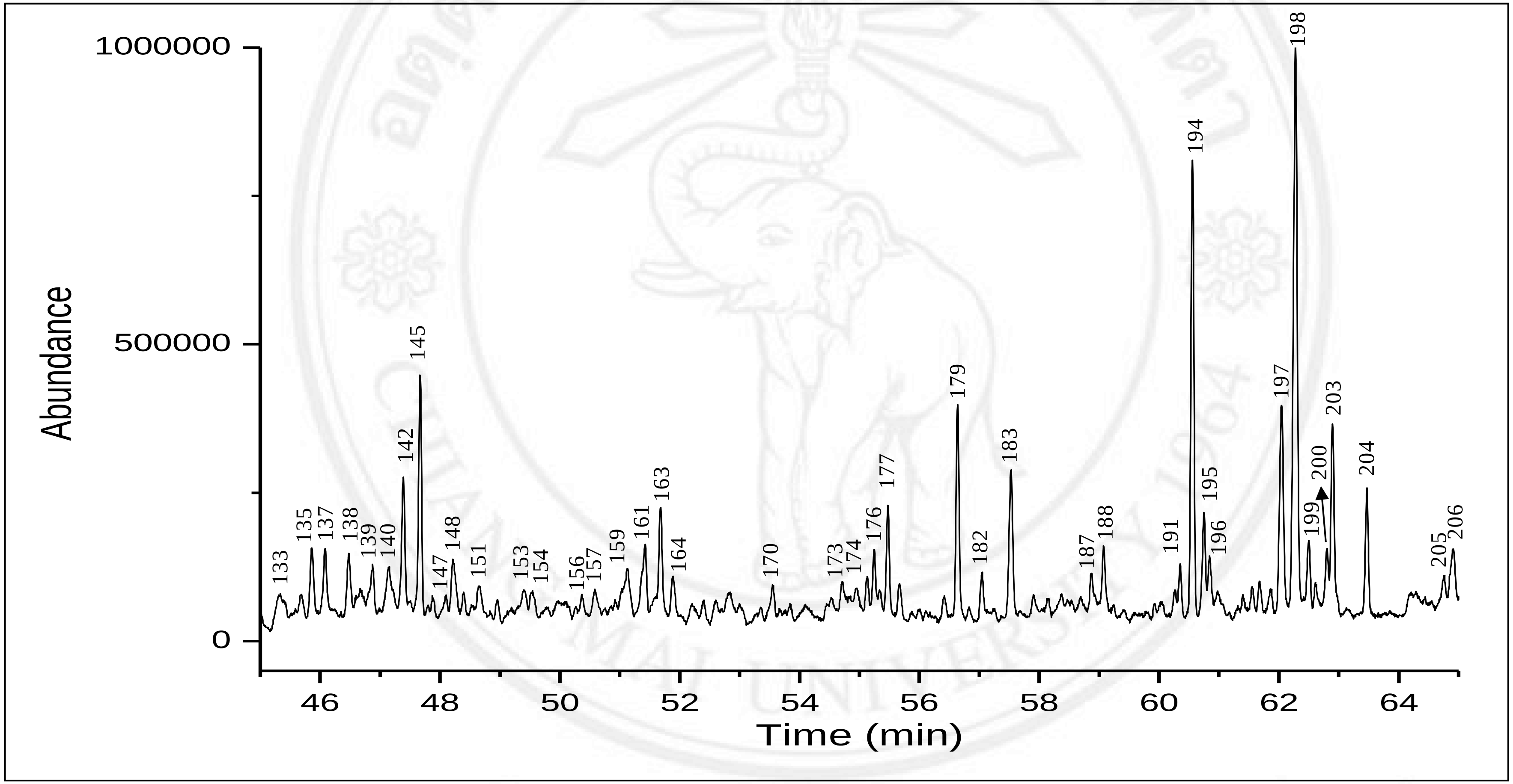

Figure 3.22 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued)

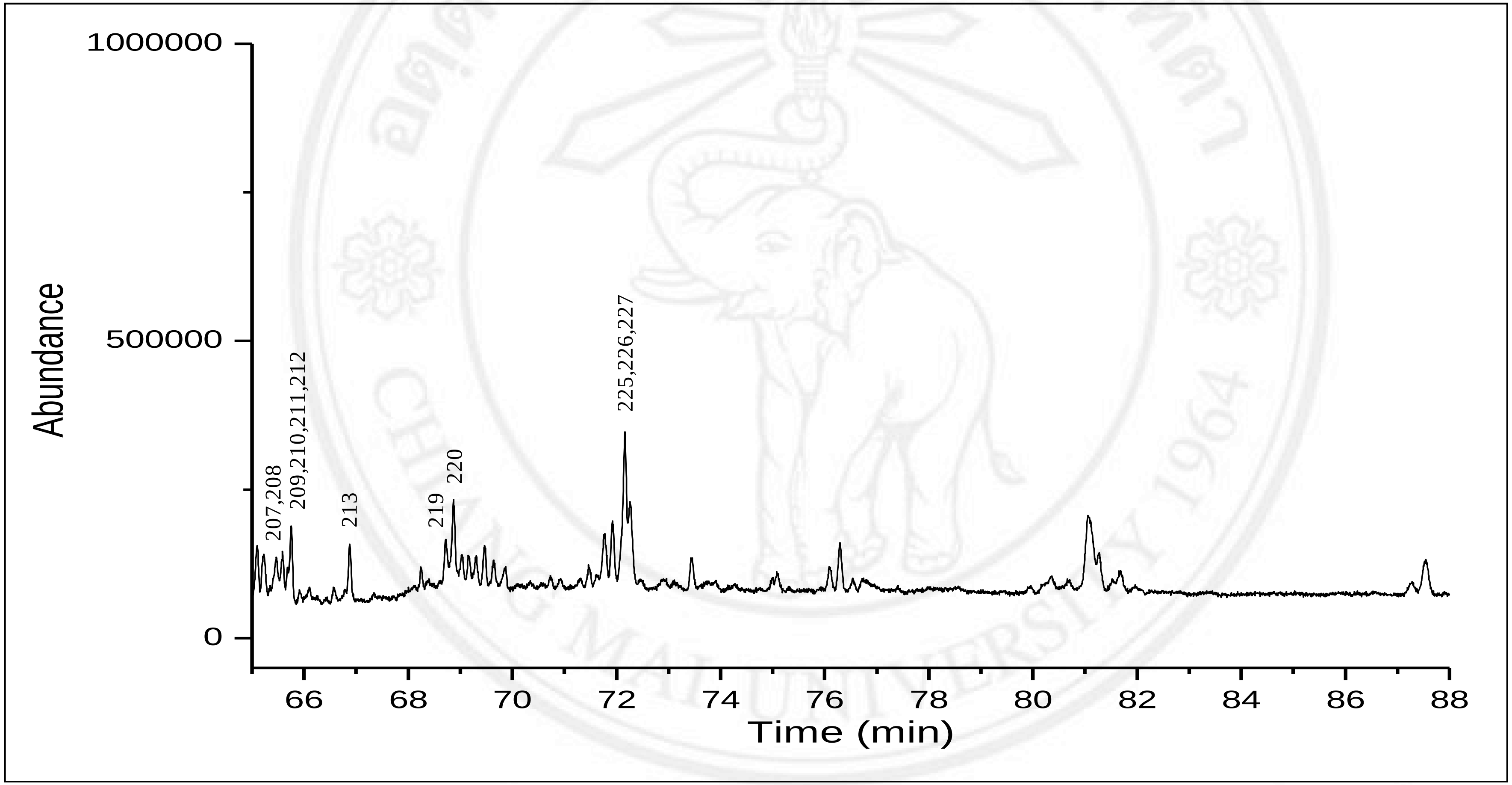

Figure 3.22 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued**)**

GC-MS chromatogram of the top layer of the bio-oil obtained by using pyrolysis temperature of 400 °C and heating rate of 10 °C/min are shown in Figure 3.22 and listed in Table 3.1. The result showed that the major compounds of the bio-oil were hydrocarbons, as well as phenolics, including phenol, cresols and xylenols. The major components were phenol, 2,4,6-trimethylpyridine, 4-methylphenol, 4-ethylphenol, pentadecane, 3,7,11,15-tetramethyl-2-hexadecen-1-ol, caffeine and nonamide.

Obviously, hydrocarbons occuplied about 30% of the bio-oil, which mostly belong to aliphatic hydrocarbons in the series of C12-C18 that were 1-dodecene, dodecane, 1-tridecene, tridecane, 1-tetradecene, tetradecane, 1-pentadecene, pentadecane, 1-hexadecene, hexadecane, 1-heptadecene, heptadecane, 1-octadecene, octadecane. These hydrocarbons were found in high contents. Alkenes were found in higher % relative contents than alkanes and alkynes.

Most of the aromatic compounds found in the bio-oil were naphthalenes, dimethylbenzenes and alkylbenzenes while *N*-,*O*-heterocyclic derivatives were pyridines, pyrazines, indoles and furans. The presence of these aromatics and oxygenated compounds such as phenolics and ketones, was attributable to its biopolymer textures such as cellulose and hemicelluloses which are the main components of biomass.[37] In addition, phenolics were produced from the degradation of lignin.[38]

From Table 3.1, the compounds including nonamide, N-methylvaleramide, allyl dodecyl oxalate, 2-methyl nonadecane, were found only at heating temperature of 400 °C not found in other top layer bio-oil samples.

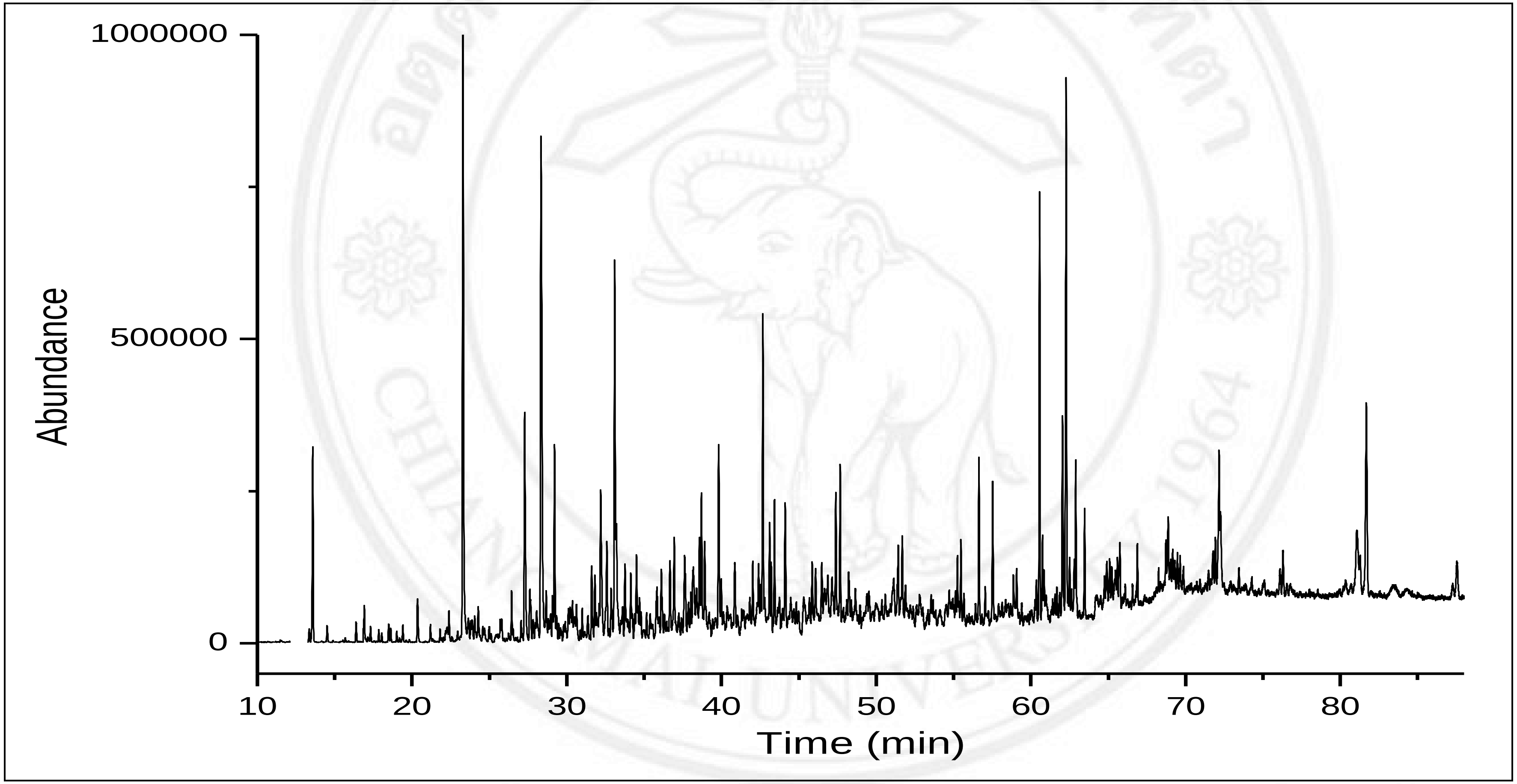

Figure 3.23 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min

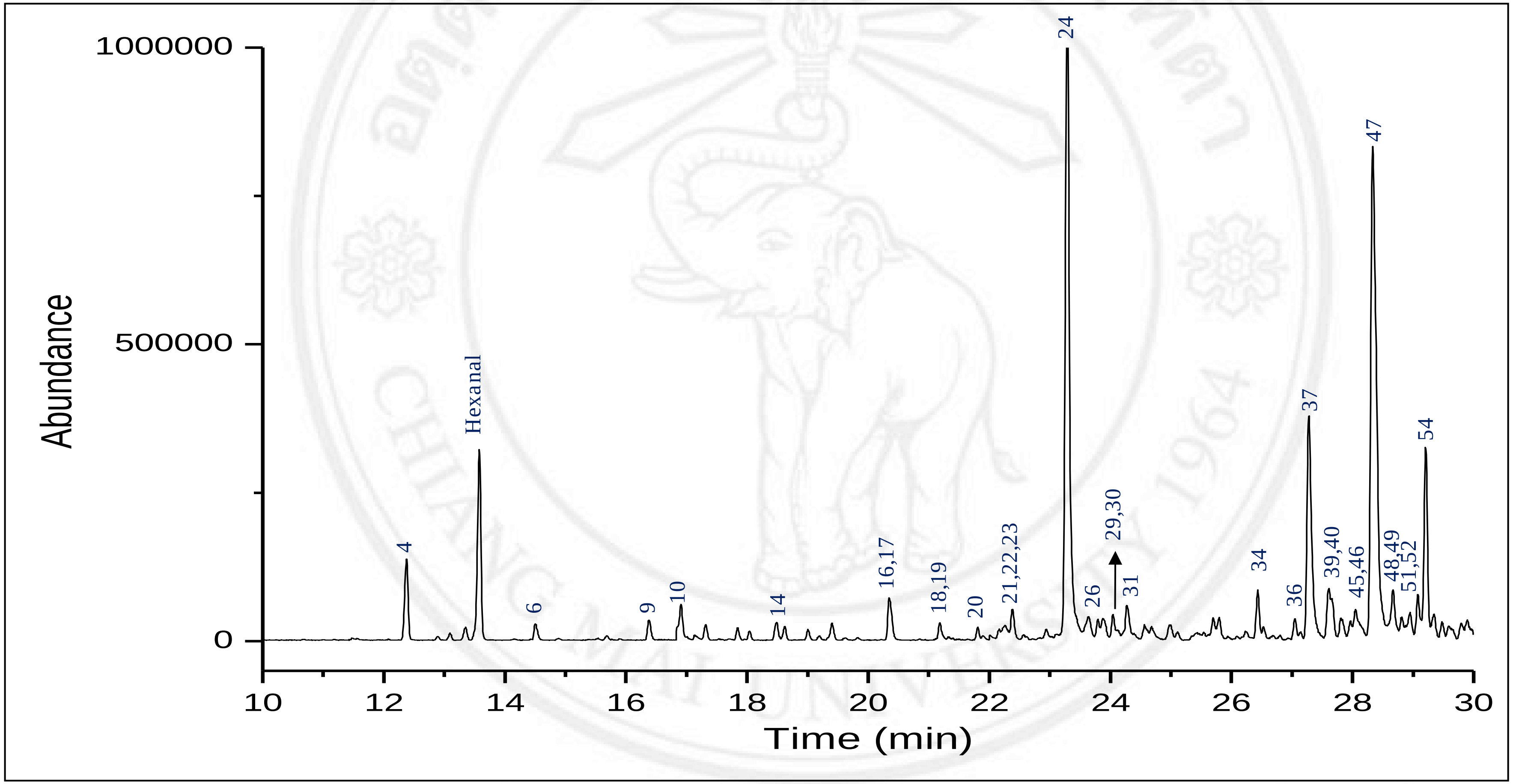

Figure 3.23 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

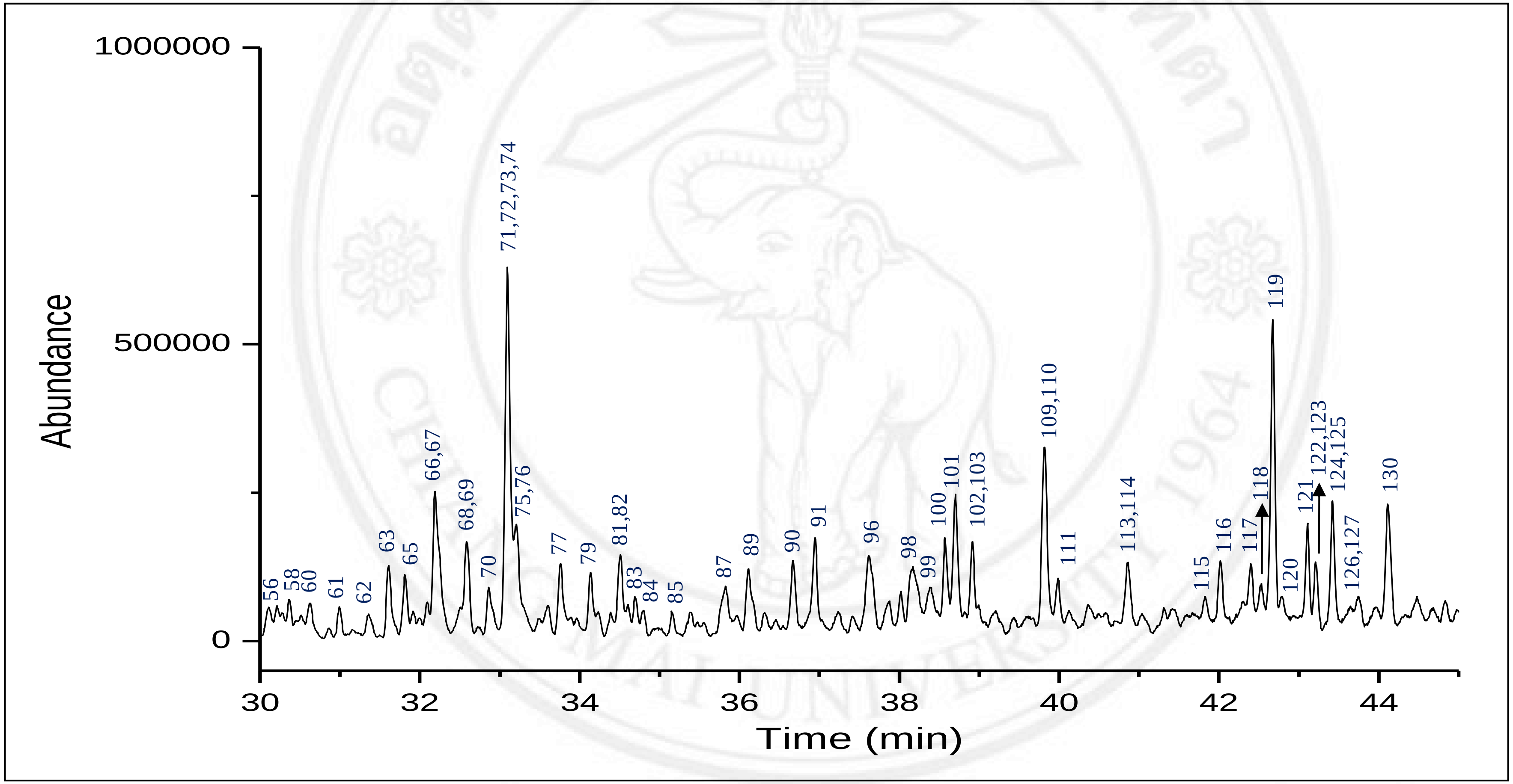

Figure 3.23 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

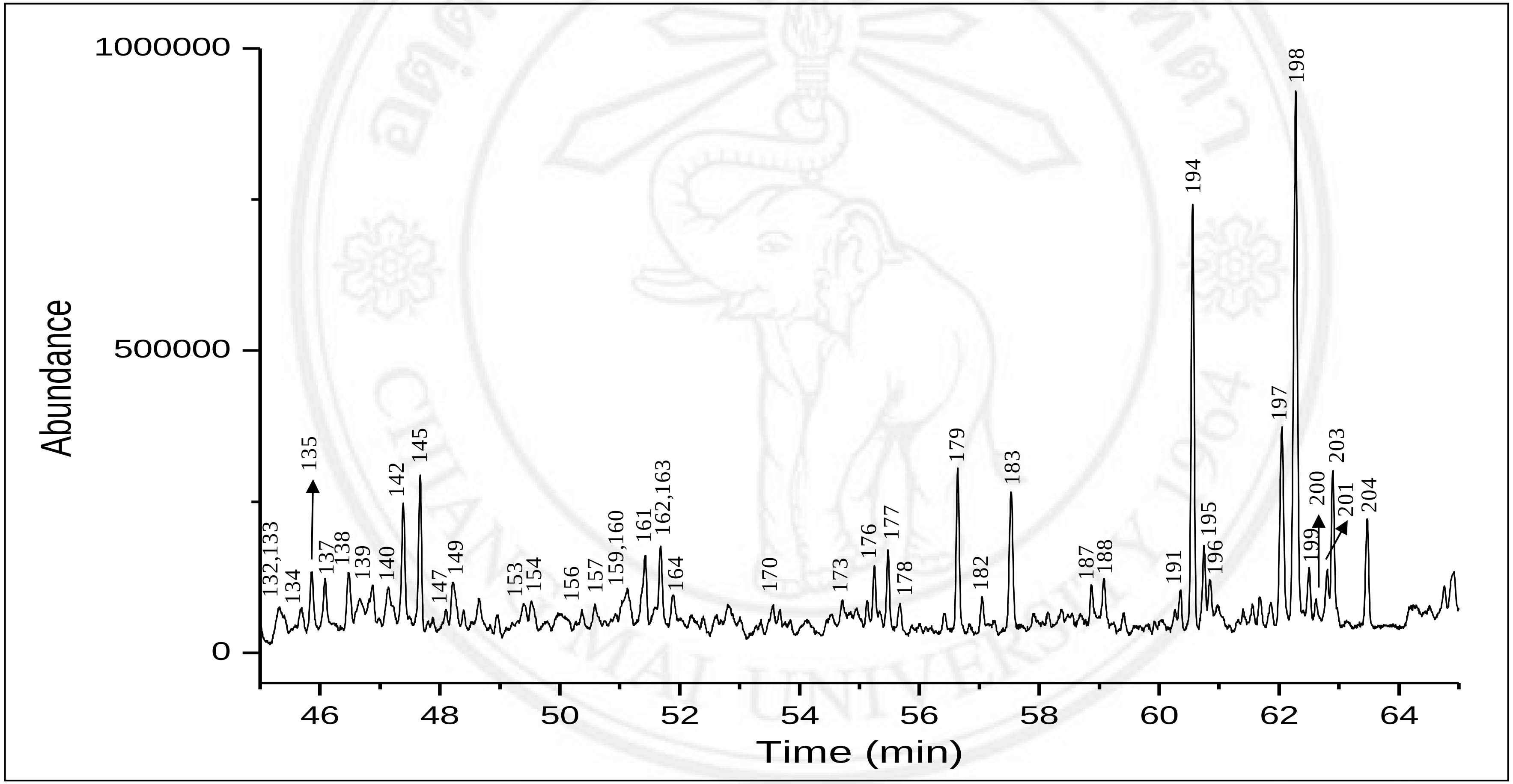

Figure 3.23 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

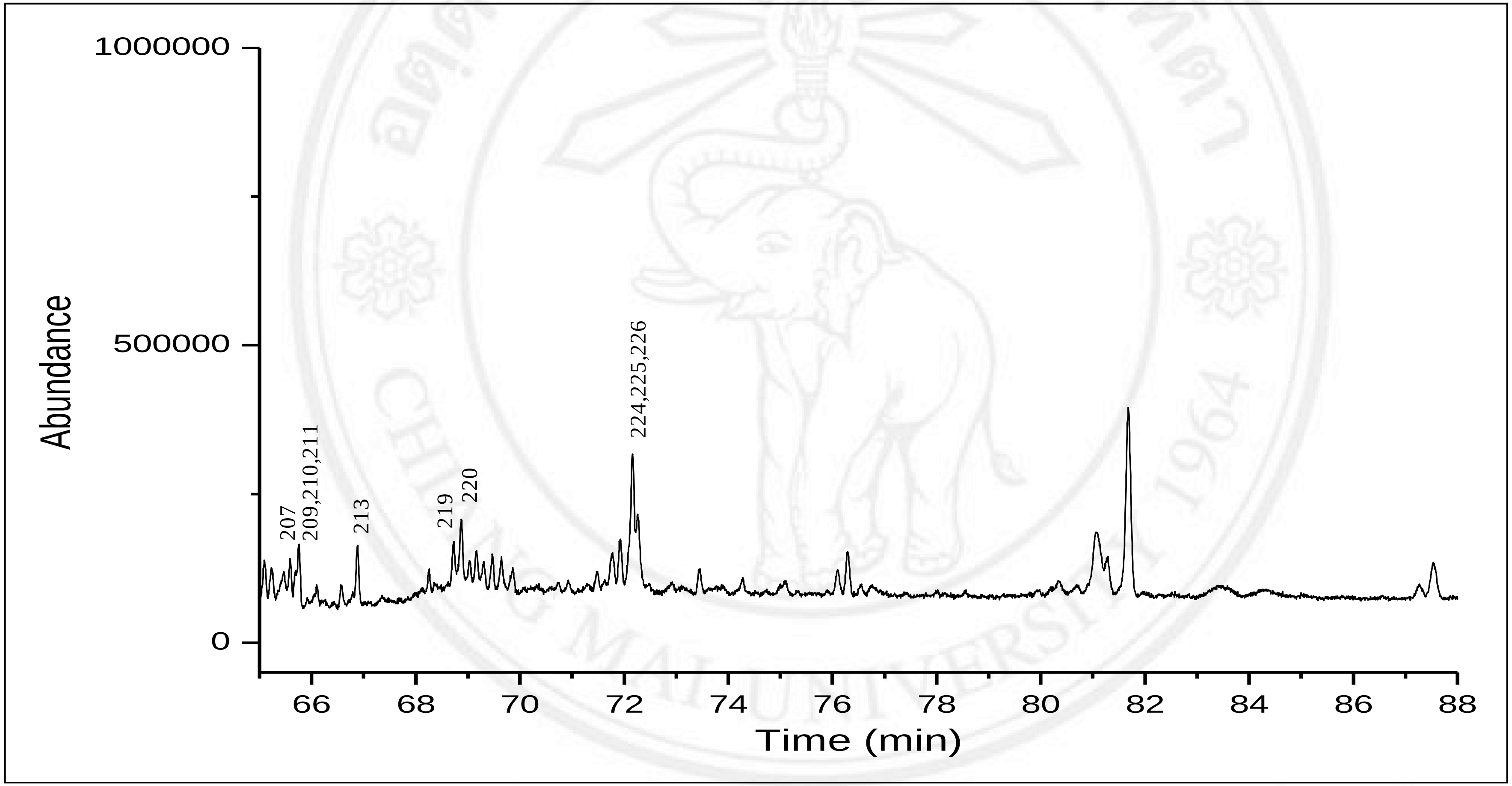

Figure 3.23 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

The bio-oil components obtained using pyrolysis temperature 500 °C and heating rate 10 °C /min are shown in Figure 3.23. The identified compounds are listed in Table 3.1. They showed that the major groups of bio-oil were hydrocarbons, phenolics and aromatic compounds.

At heating rate 10 °C /min, the organic compounds that found in the top layer at temperature 400 °C but not found at temperatures 500 °C and 600 °C were 2-methyl-2-pentanol, 3-methyl-3-pentanol, 5-hexen-2-one, 2-methylcyclopentanone, 3-methylcyclopentanol, cyclohexanol, 2-cyclohexen-1-one, 2-ethyl-6-methylpyrazine and 1-methyl-2-n-hexylbenzene.

The organic components including nonamide, N-methylvaleramide, allyl dodecyl oxalate and 2-methylnonadecane were found only in the bio-oil obtained at 400 °C and heating rate 10 °C/min, but not found in other top layer of bio-oil samples.

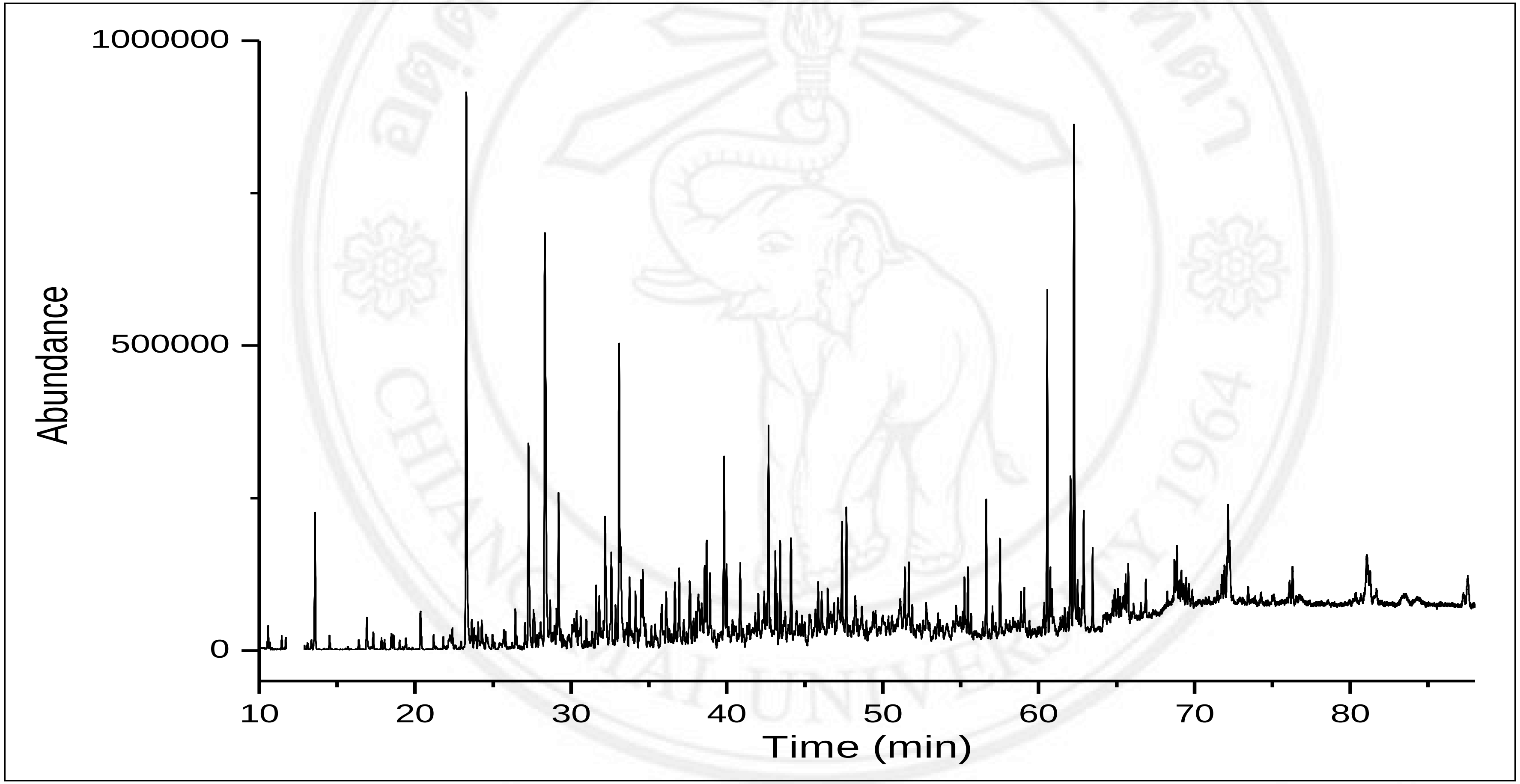

Figure 3.24 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min

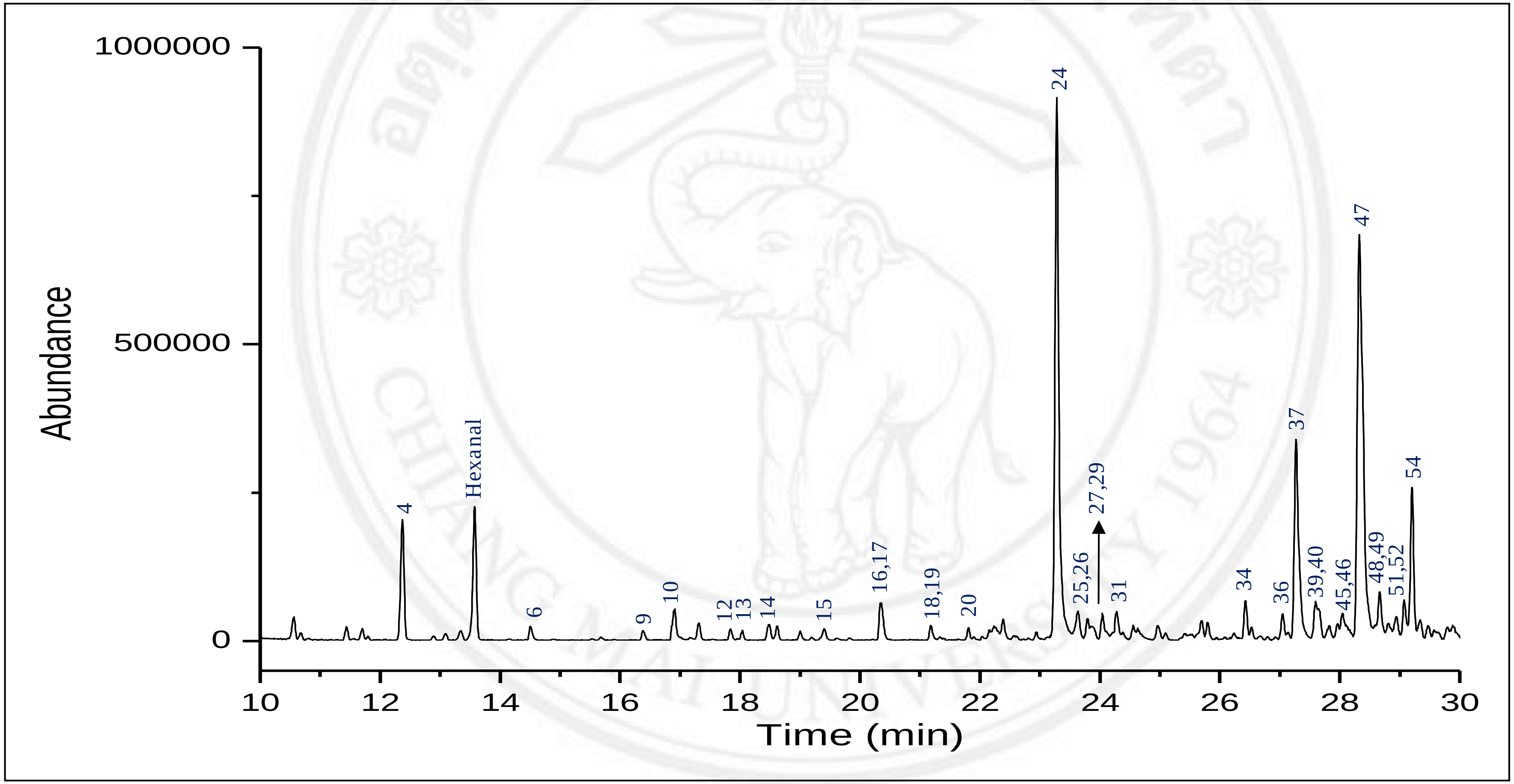

Figure 3.24 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min (continued)

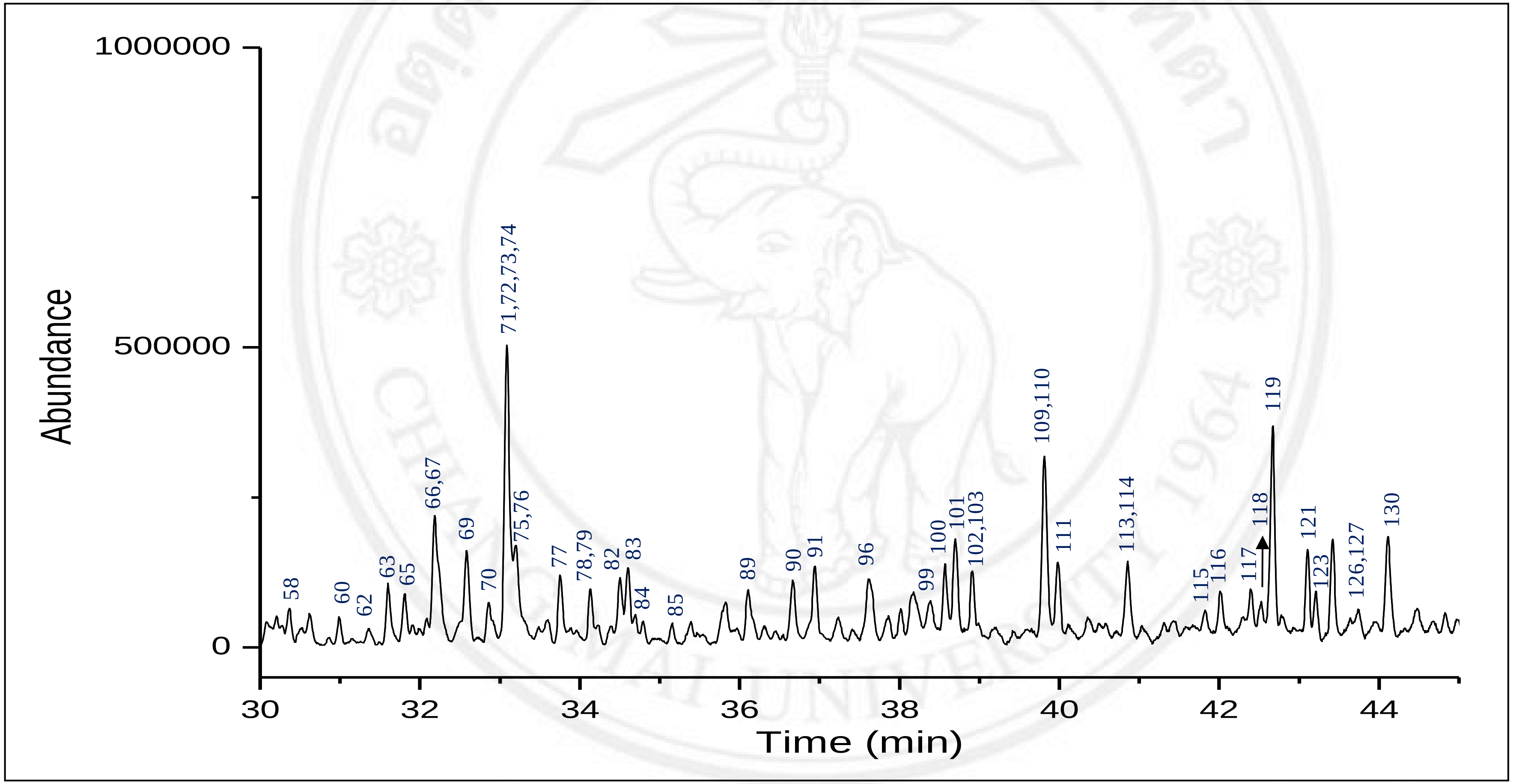

Figure 3.24 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min (continued)

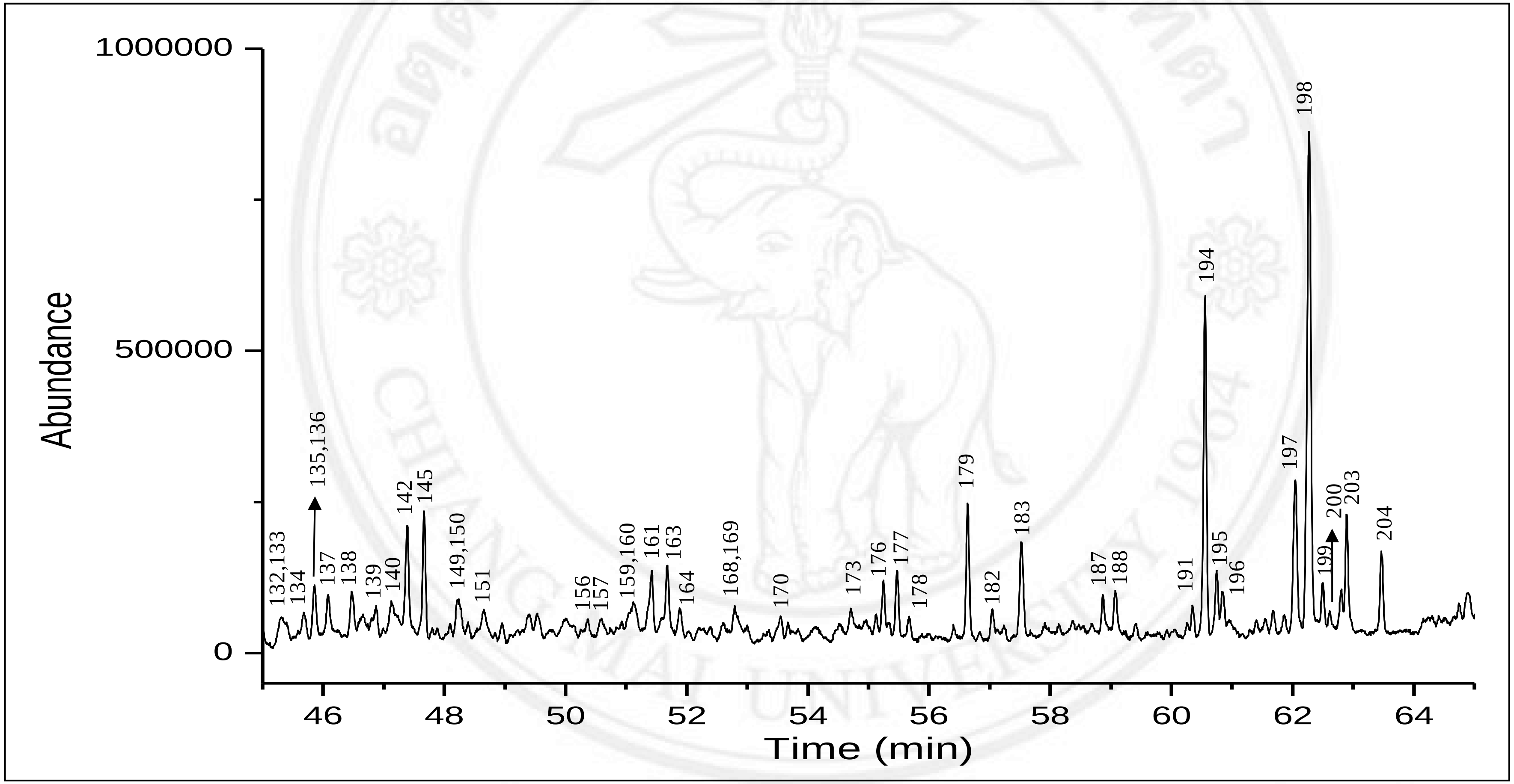

Figure 3.24 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min (continued)

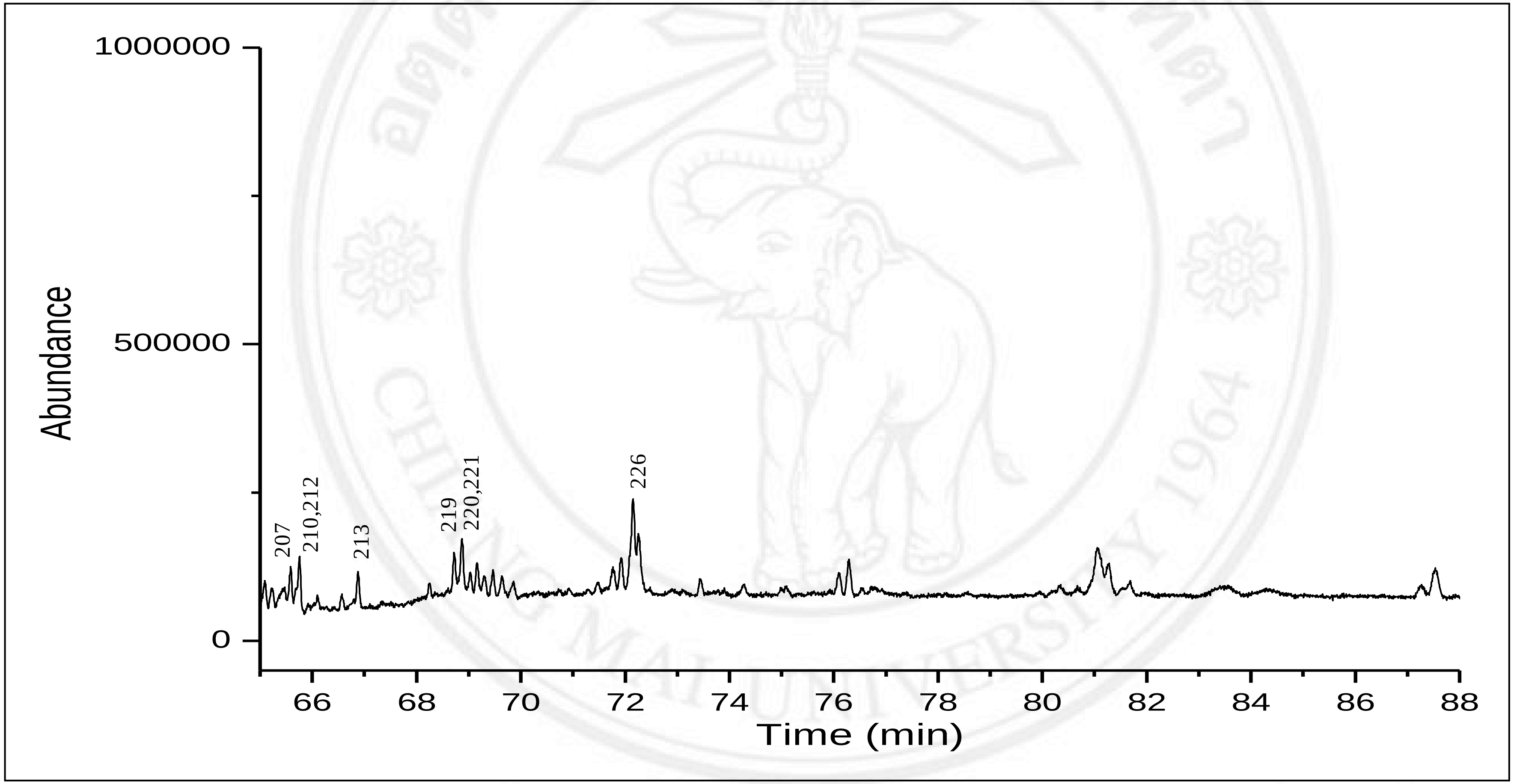

Figure 3.24 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min (continued)

As can be seen in Figure 3.24, GC-MS chromatograms of top layer bio-oil pyrolyzed at temperature of 600 °C and heating rate of 10 °C/min were demonstrated. The results indicated that the major products of bio-oil were phenolics and hydrocarbons, as same as pyrolysis at temperatures 400 °C and 500 °C. The same pattern of these organic compounds, phenolics and hydrocarbons, were also found in the top layer bio-oil samples.

At the same heating rate 10 °C/min, the pyrolysis temperatures of 400 °C, 500 °C and 600 °C were not quite different in their organic components. However, the pyrolysis temperatures had much effect on the content of organic compounds.

The organic components found only in the bio-oil pyrolysed at temperature 600 °C was 1-methylheptylbenzene. Otherwise, the components including 1-methyl-3-(1-methylethyl)benzene, 3,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine, 2-ethylidene cyclohexanone, 1-heptyl-2-methylcyclopropane, 2-methyloctadecane, 2-(1-methylethyl) naphthalene and heptacosane, were found at the temperatures 400 °C and 500 °C but not found at the temperature 600 °C.

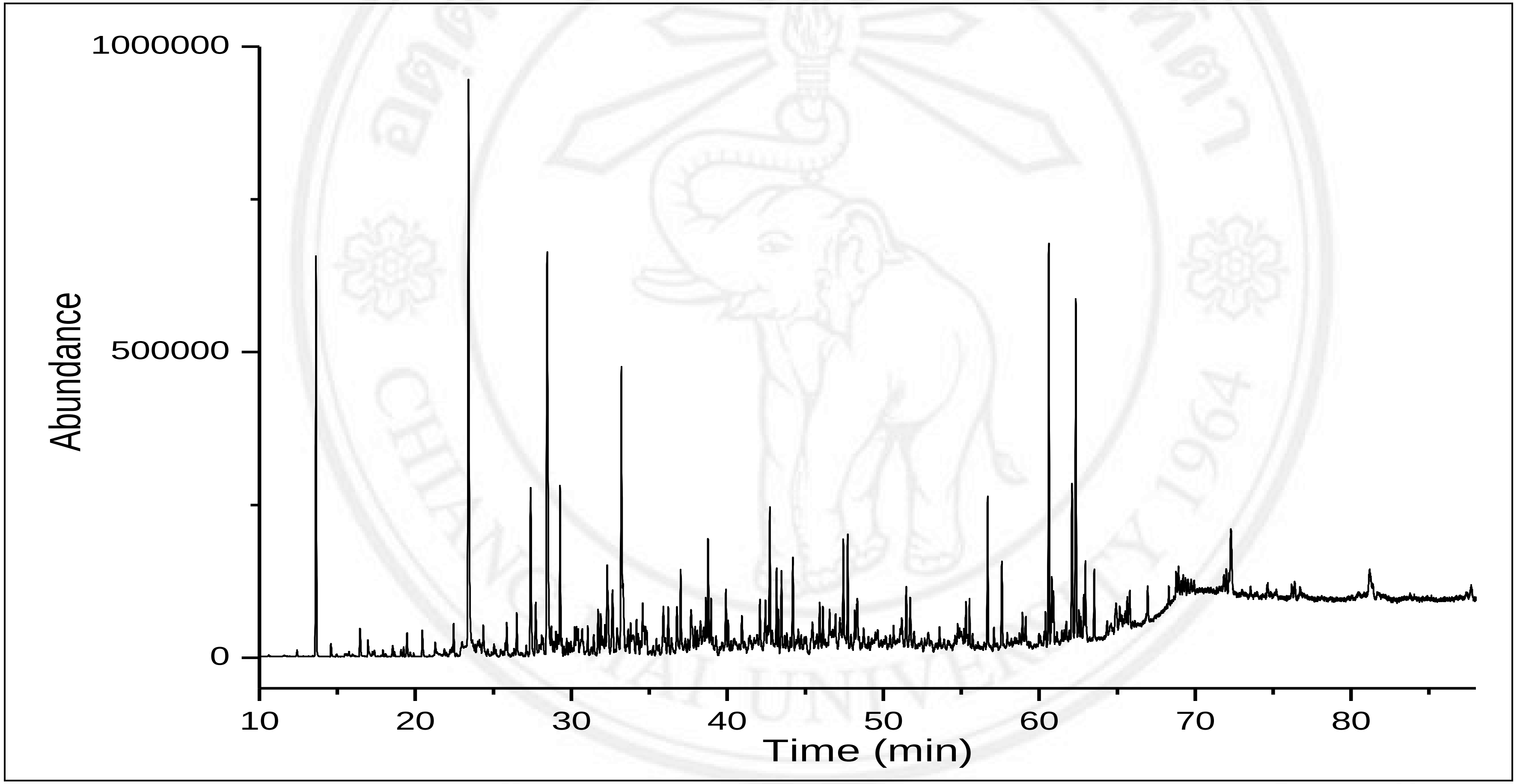

Figure 3.25 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min

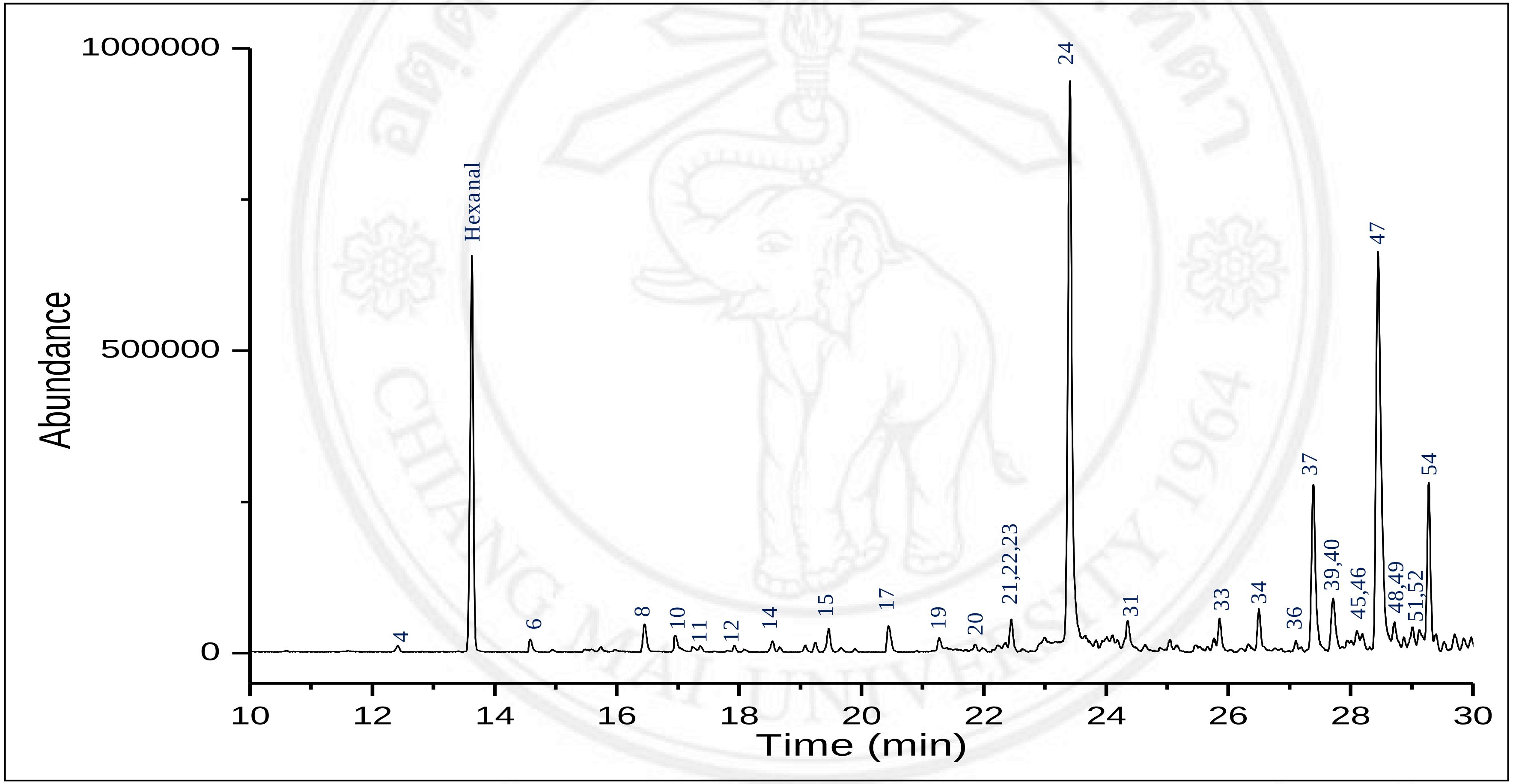

Figure 3.25 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

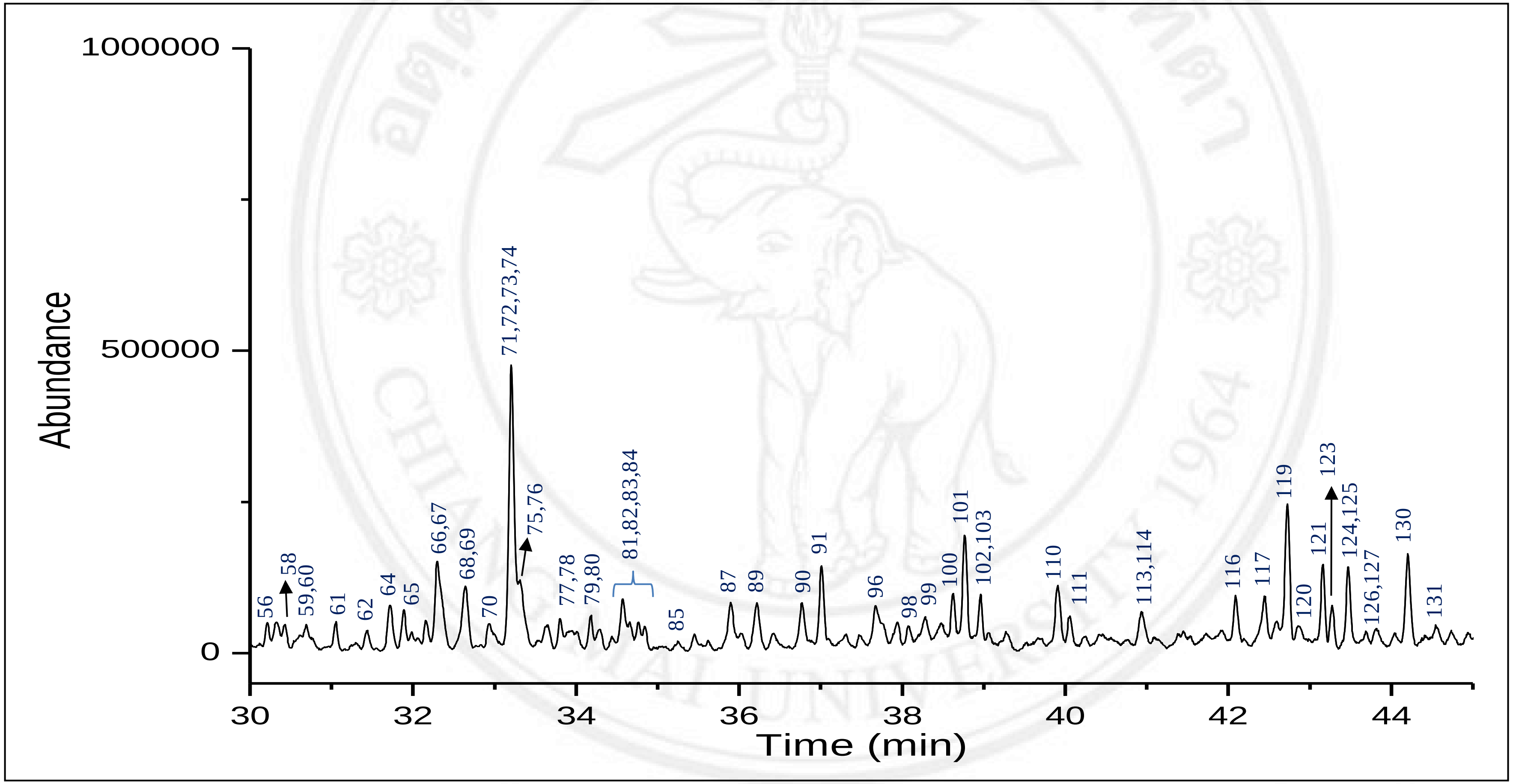

Figure 3.25 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

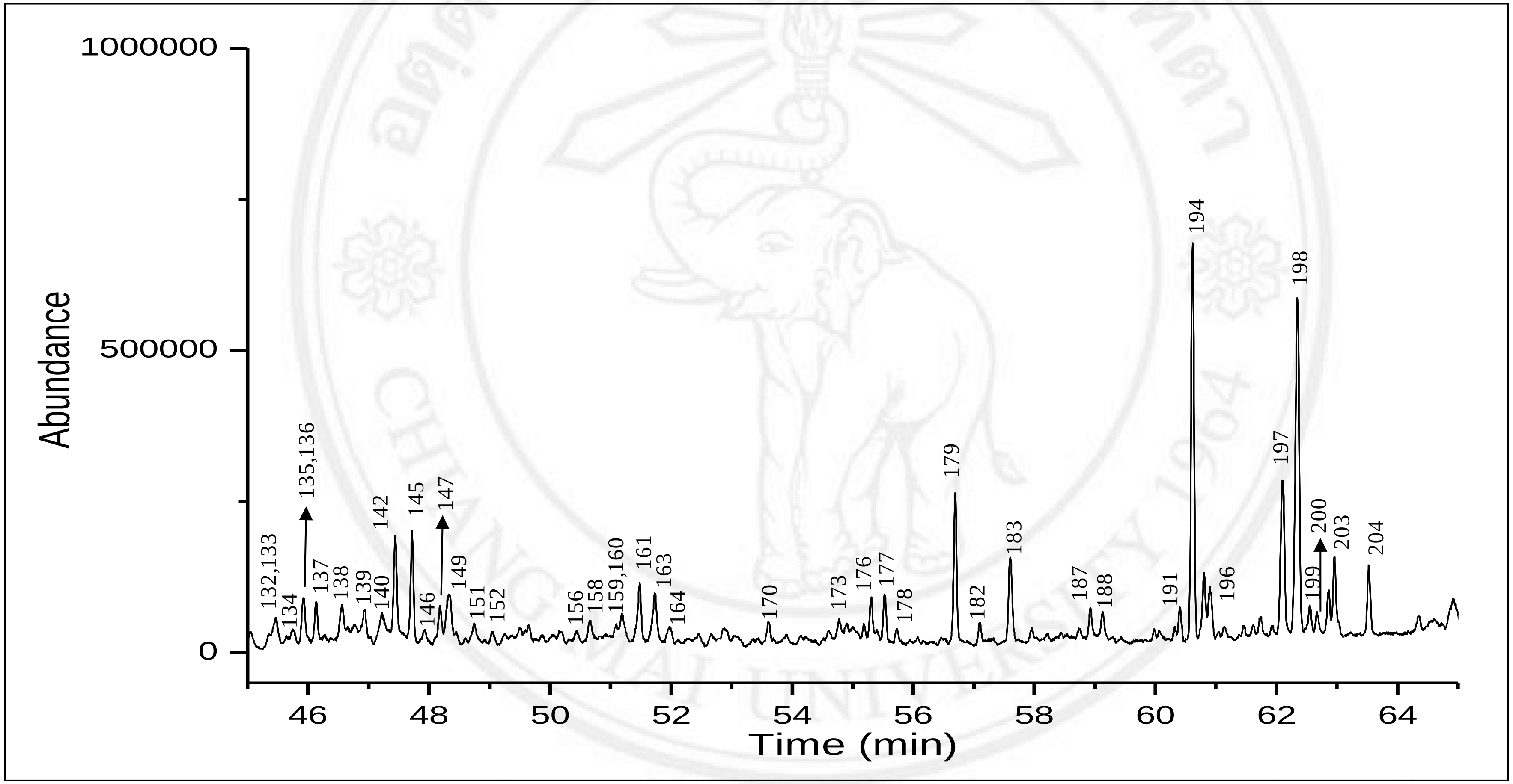

Figure 3.25 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

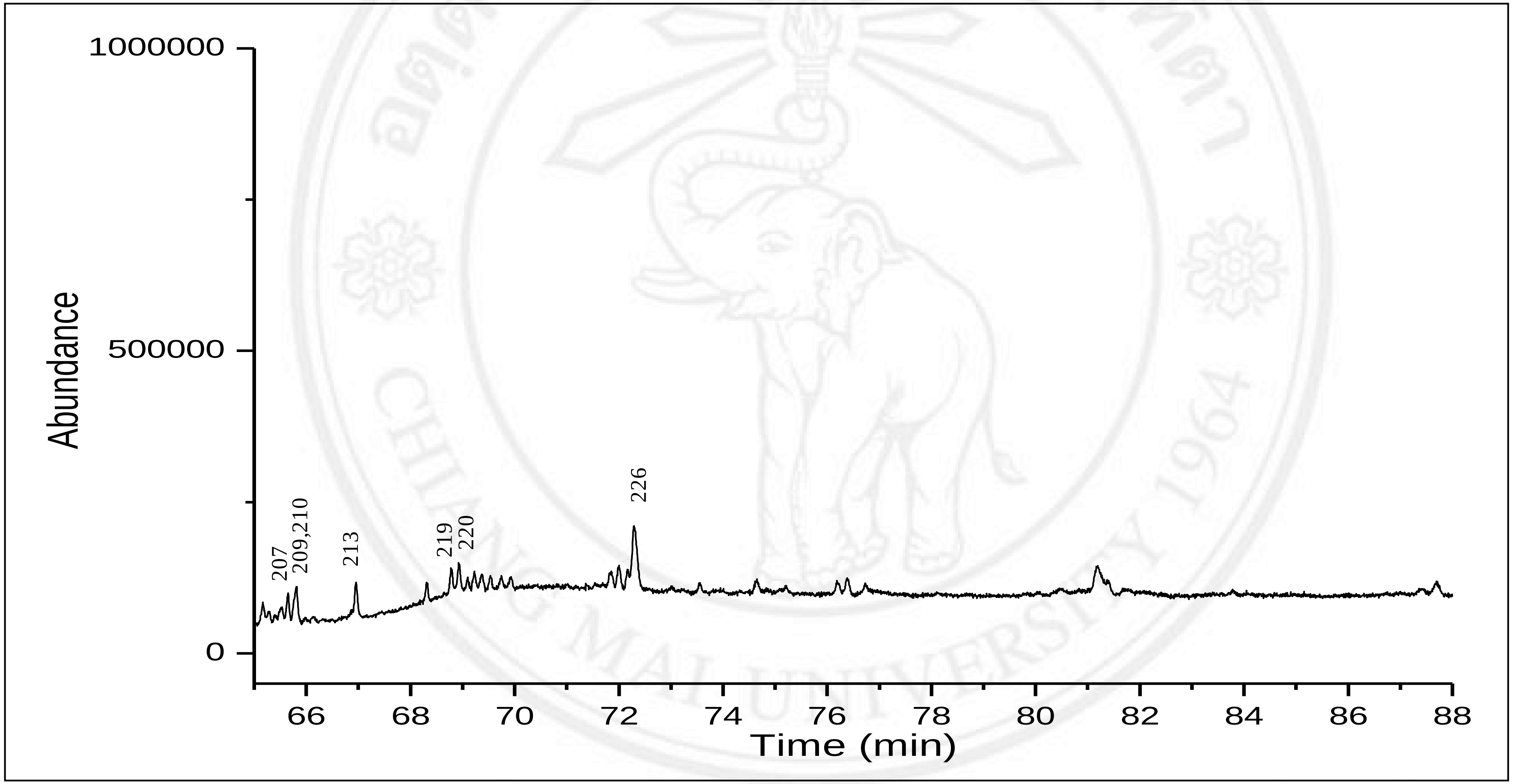

Figure 3.25 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

The organic components of the top layer of bio-oil pyrolysed at temperature 400 °C and heating rate 50 °C/min are shown in Figure 3.25. The bio-oil components that were found as major compounds such as phenol, 4-methylphenol, 4-ethylphenol, 2-butyl-2-octenal, 3,7,11,15-tetramethyl-2-hexadecen-1-ol and caffeine. The organic components including 3-methylcyclopentanol and 1-heptyl-2-methylcyclopropane were found only at 400 °C, not found at 500 °C and 600 °C.

Comparison of the bio-oils pyrolysed at 400 °C using heating rate of 10 °C/min and 50 °C/min, revealed that the organic components found at heating rate 10 °C/min but not found at heating rate 50 °C/min were 2-methyl-2-pentanol, 3-methyl-3-pentanol, 5-hexen-2-one, 2-methylcyclopentanone, 2-furanmethanol, cyclohexanol, 2,4,6-trimethyl pyridine, 1-methyl-3-(1-methylethyl)benzene, 1,13-tetradecadiene, 3,7,11,15-tetramethyl-2-hexadecene and nonamide. Whereas, the organic compounds found at heating rate 50 °C/min but not found at heating rate 10 °C/min were 1-dodecene, 2,3-dihydro-1H-inden-1-one, 2-ethylnaphthalene, 2,7-dimethylnaphthalene, 1,5-dimethylnaphthalene.

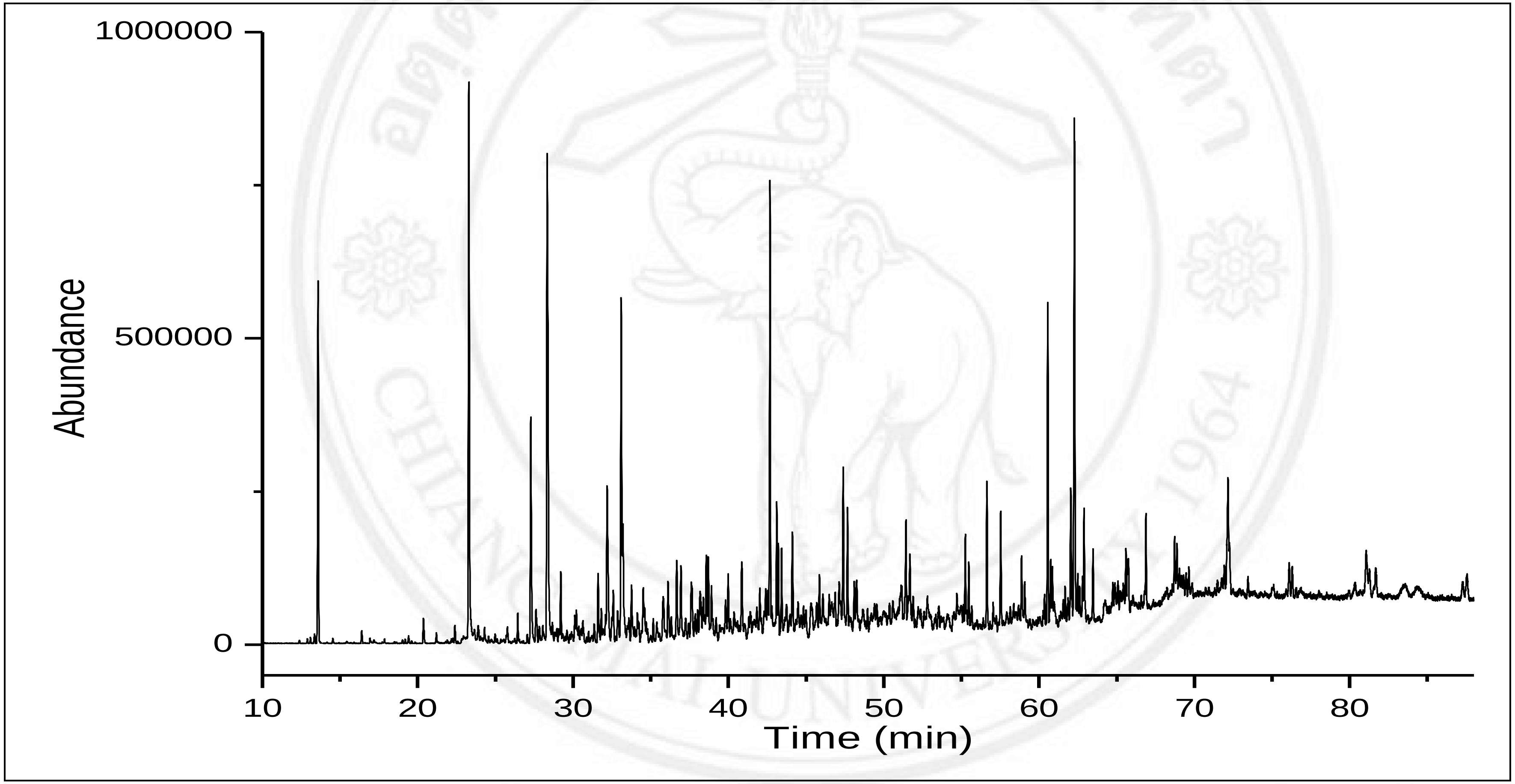

Figure 3.26 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min

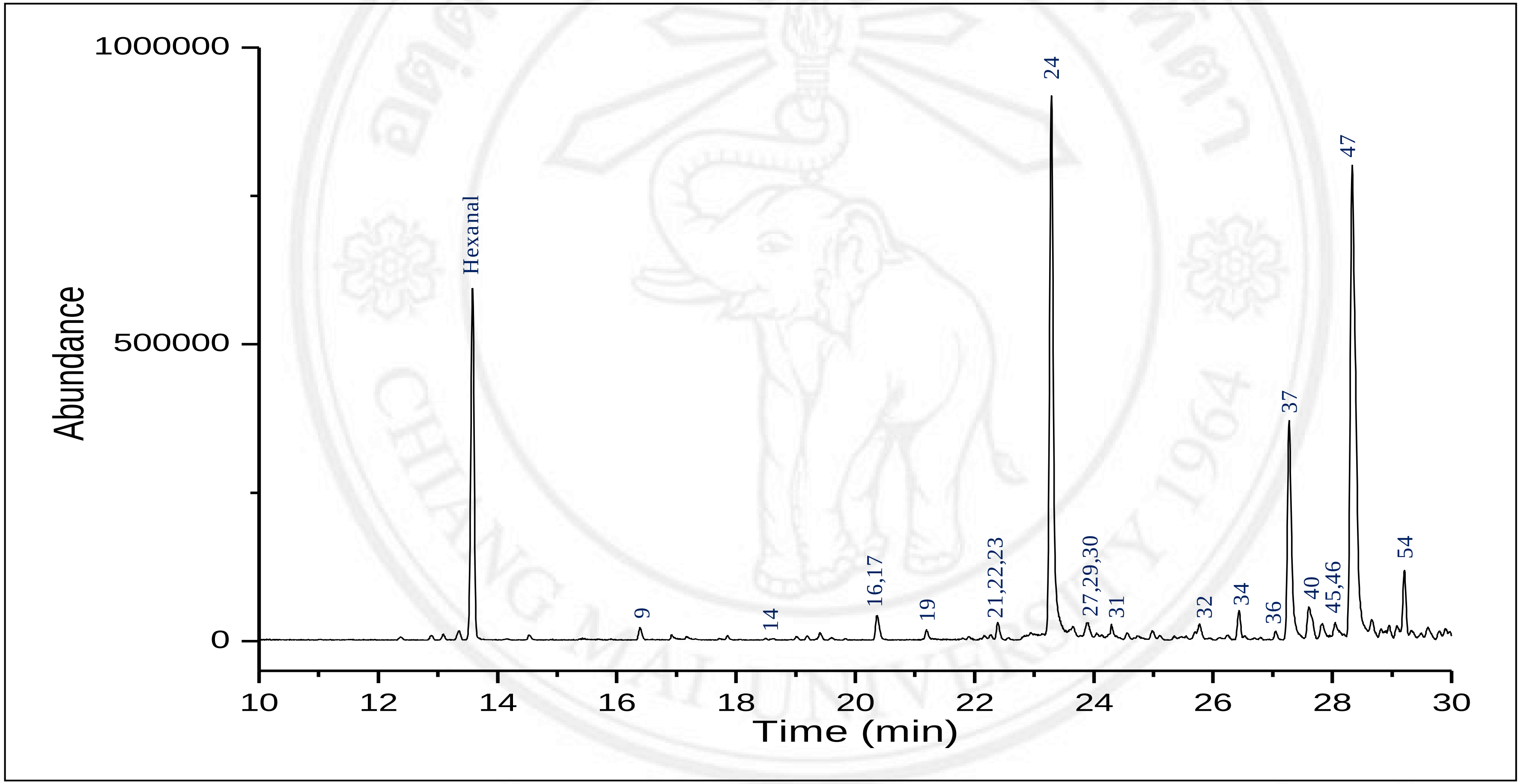

Figure 3.26 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

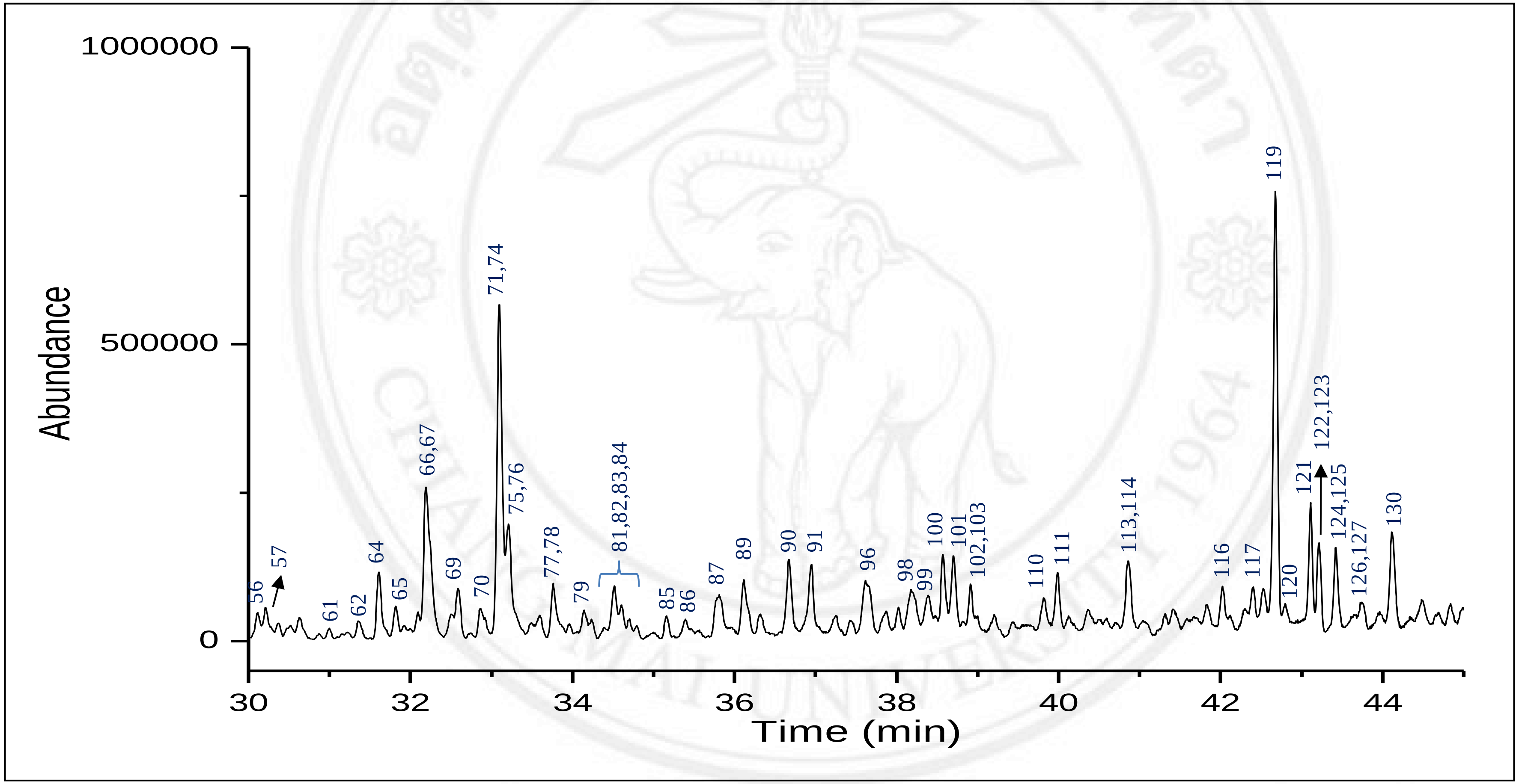

Figure 3.26 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

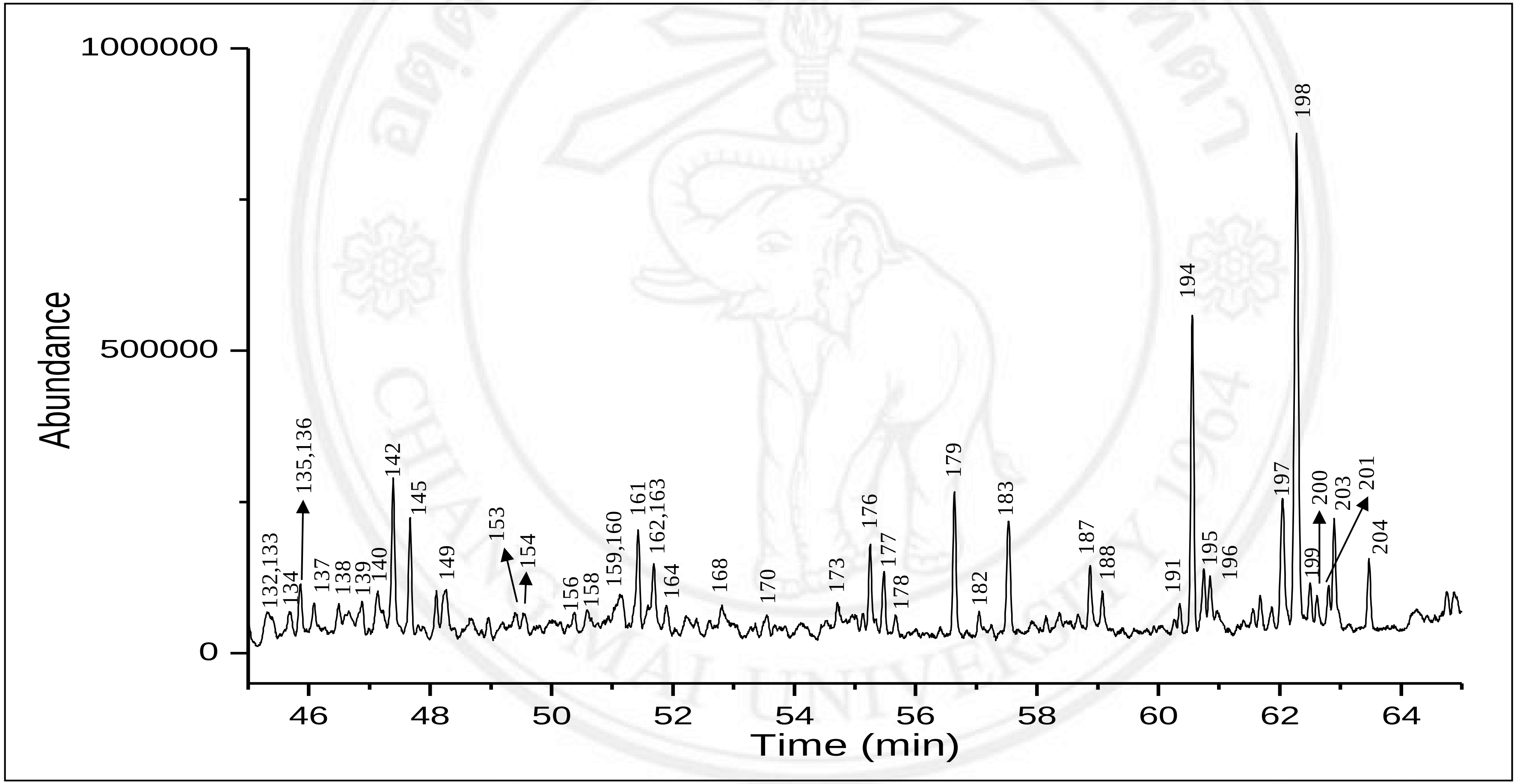

Figure 3.26 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

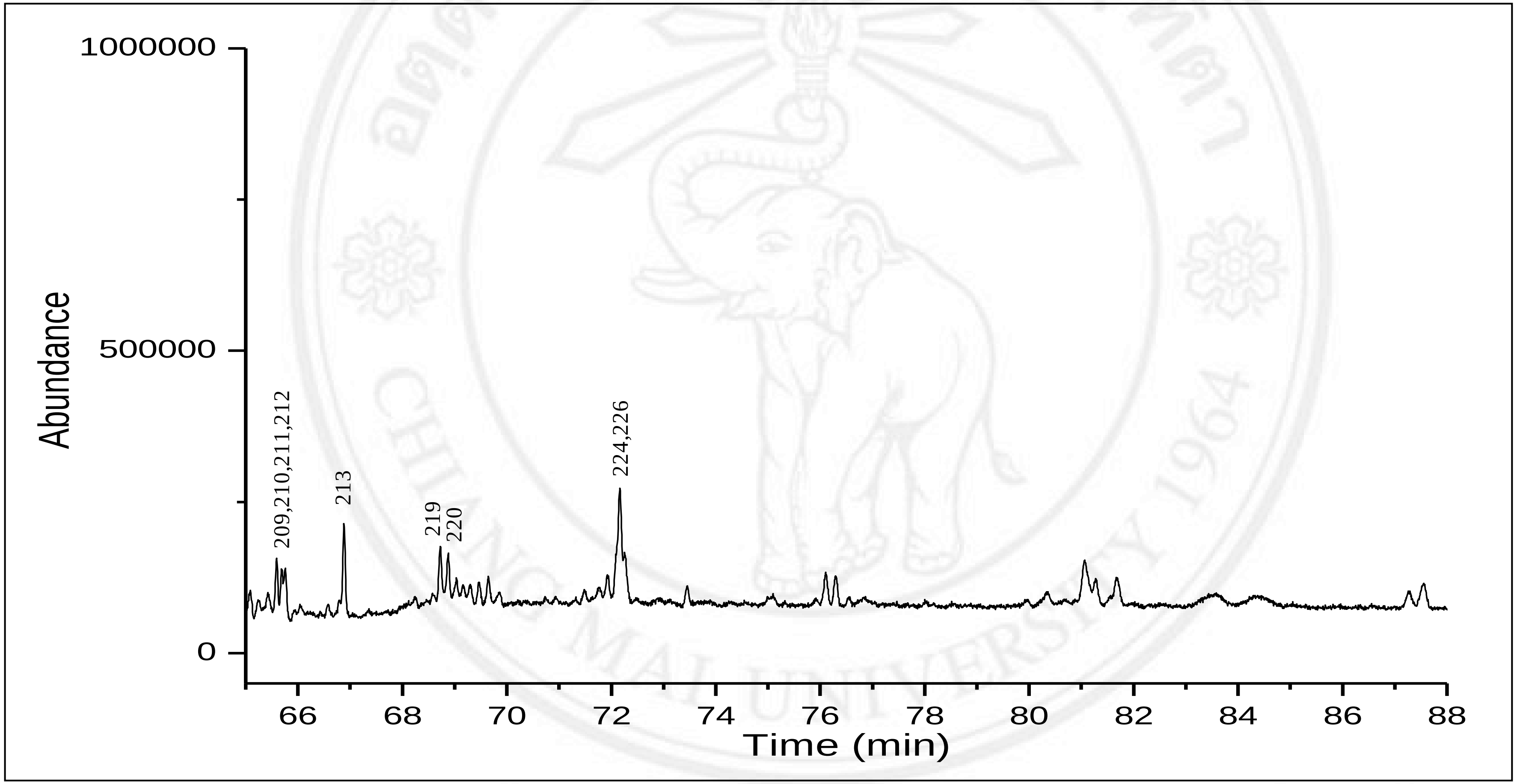

Figure 3.26 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

Figure 3.26 shows the chromatograms of the top layer of the bio-oil pyrolysed at temperature of 500 °C and heating rate of 50 °C/min. The major compounds of the bio-oil were the same as bio-oil obtained using temperature 400 °C. Their components were similar except a few.

There were two compounds, 1-ethynyl-2-methylbenzene and 2-ethyl-6-methylphenol, which were presented in this bio-oil sample but not in other top layer samples. In comparison, the organic compounds including 2-hexanone, 2-hexanol, 3-methylcyclopentanol, ethylbenzene, 1,2-dimethylpyridine, 2,6-dimethylpyridine, 3,5-dimethylpyridine, 2-ethyl-6-methylpyrazine, (1-methylpropyl)benzene, 1-(1H-pyrrol-2-yl)ethanone, 1-undecene, (E)-cinnamaldehyde, 2,3-cyclopentenopyridine, (E)-1-butenylbenzene, 1-heptyl-2-methylcyclopropane, 3,7-dimethyl-1-octene, 1-methyl -2-n-hexylbenzene, (1-methyldodecyl)benzene and 2-(1-methylethyl)naphthalene, were found at temperature 400 °C, but not found at 500 °C and heating rate of 50 °C/min.

It is noted that many compounds were not presented in the GC-MS chromatogram but presented in the GC×GC-MS contour plot such as 2-cyclohexen-1-one, trimethylpyrazine, 1-ethenyl-2(1H)-pyridinone, 2-ethyl-6-methylpyridine, 1-ethynyl-2-methylbenzene, acetophenone, 1-octanol, 3-ethyl-2-cyclopenten-1-one, 2-methylbenzofuran, (2-methyl-2-propenyl) benzene, 2-ethylidenecyclohexanone and 1-ethyl-2,5-pyrrolidinedione.

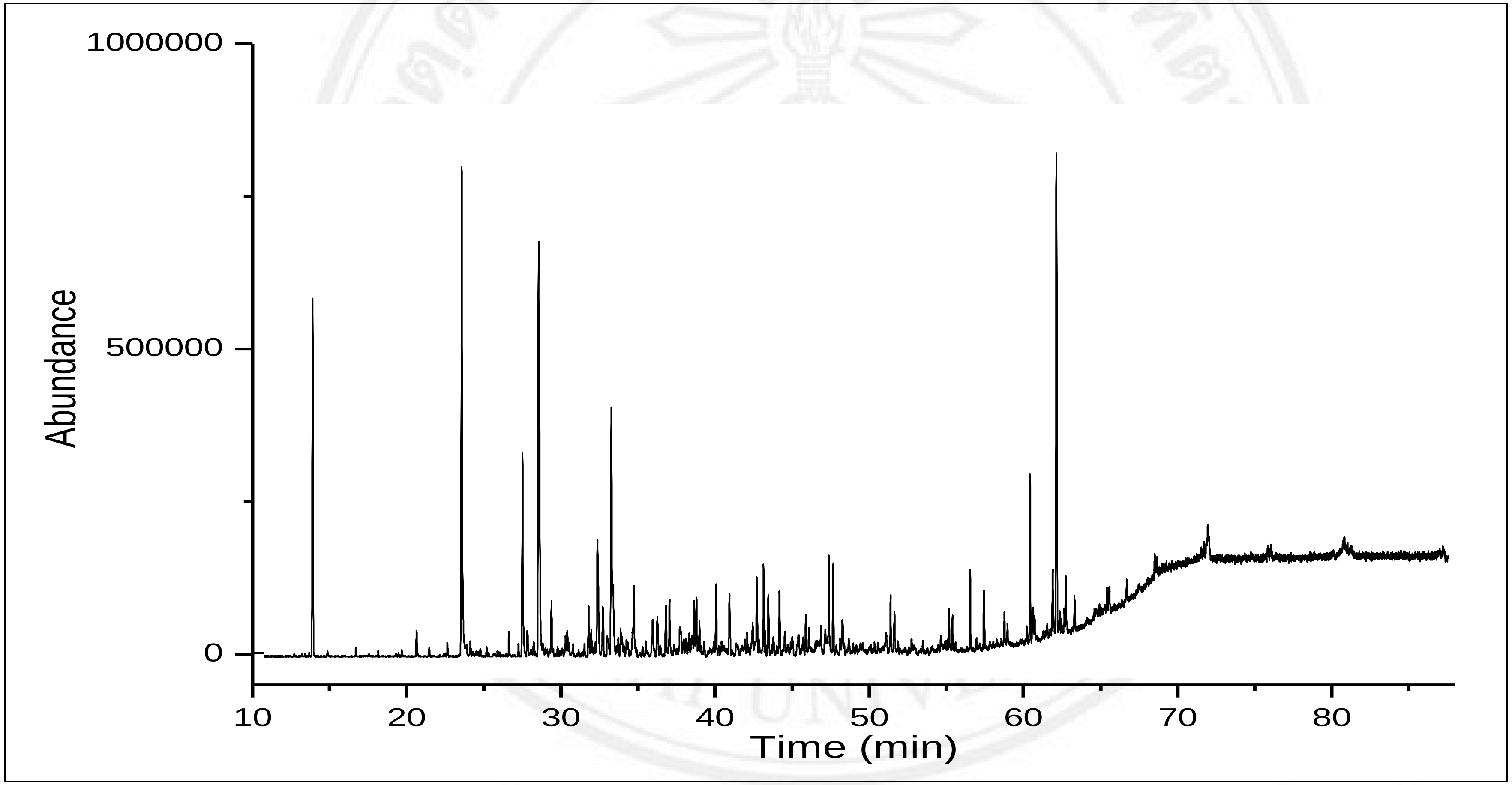

Figure 3.27 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min

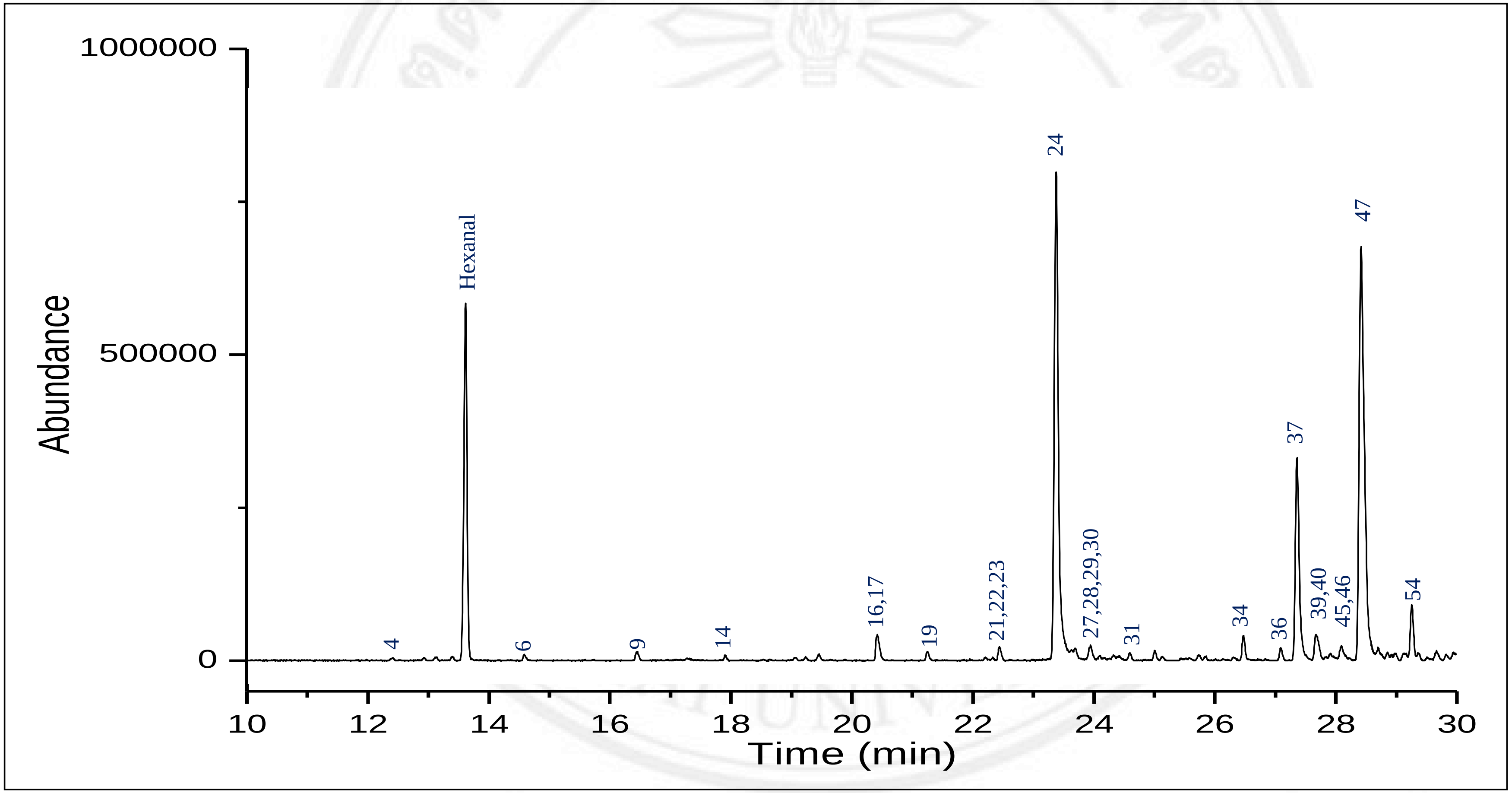

Figure 3.27 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min (continued)

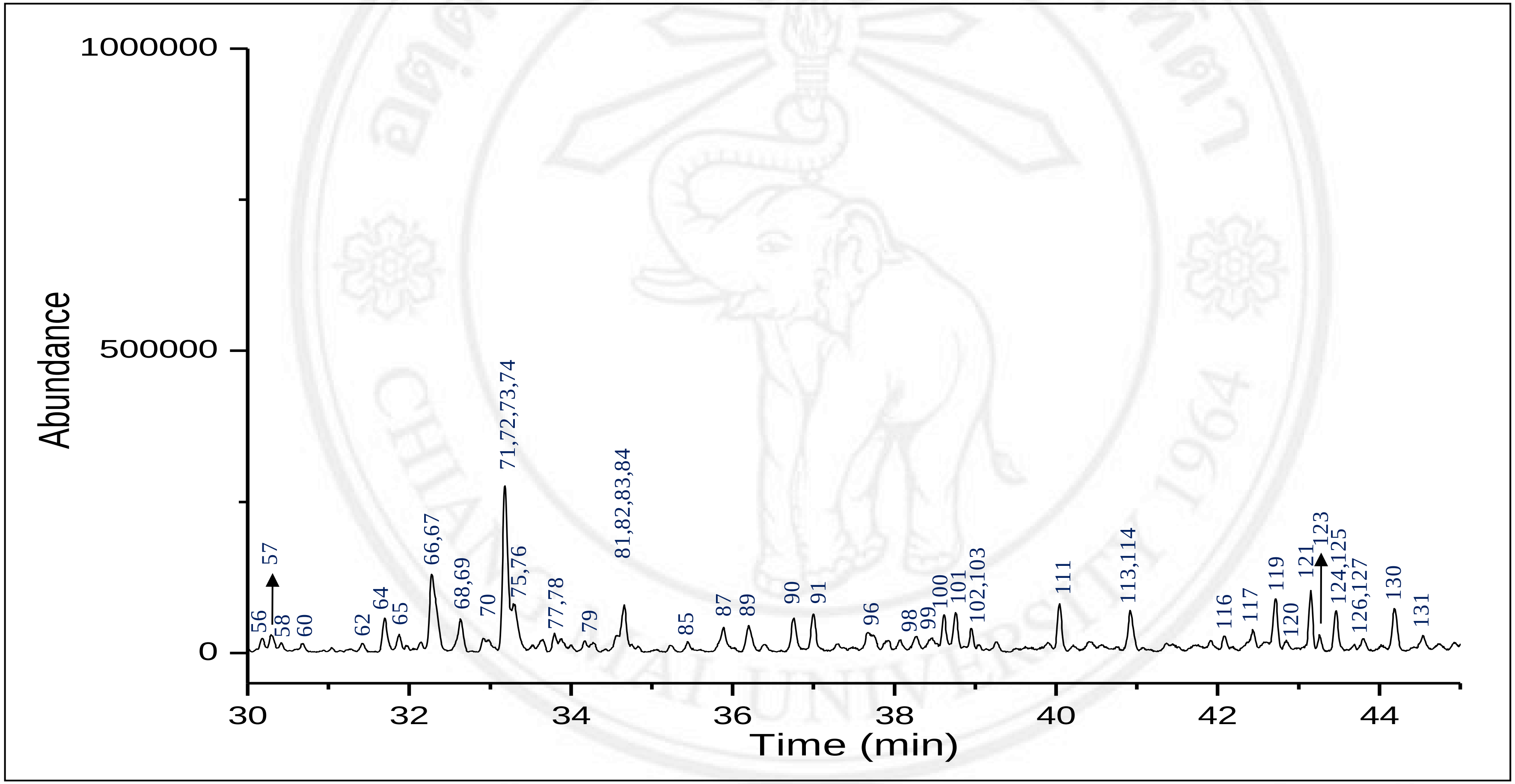

Figure 3.27 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min (continued)

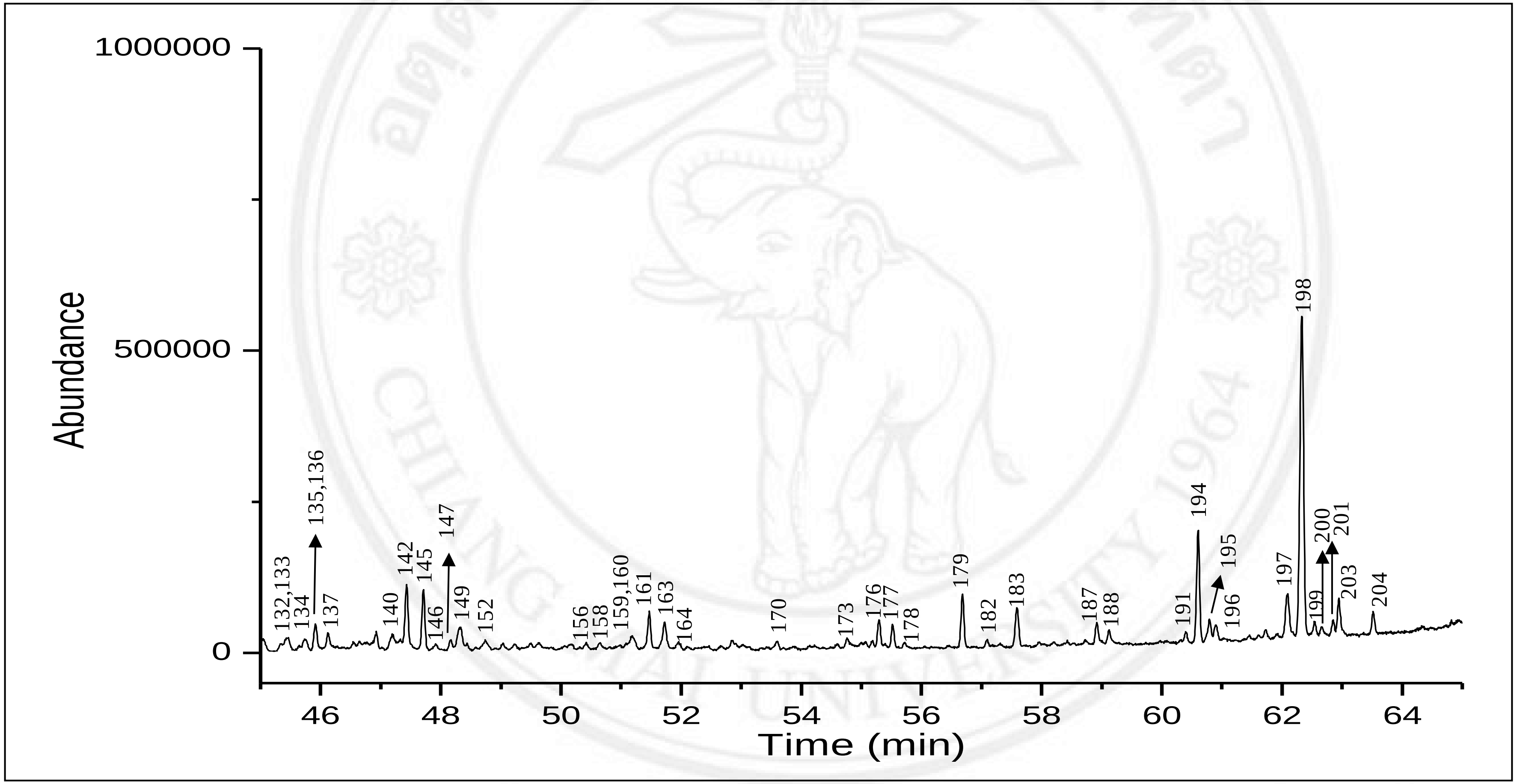

Figure 3.27 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min (continued)

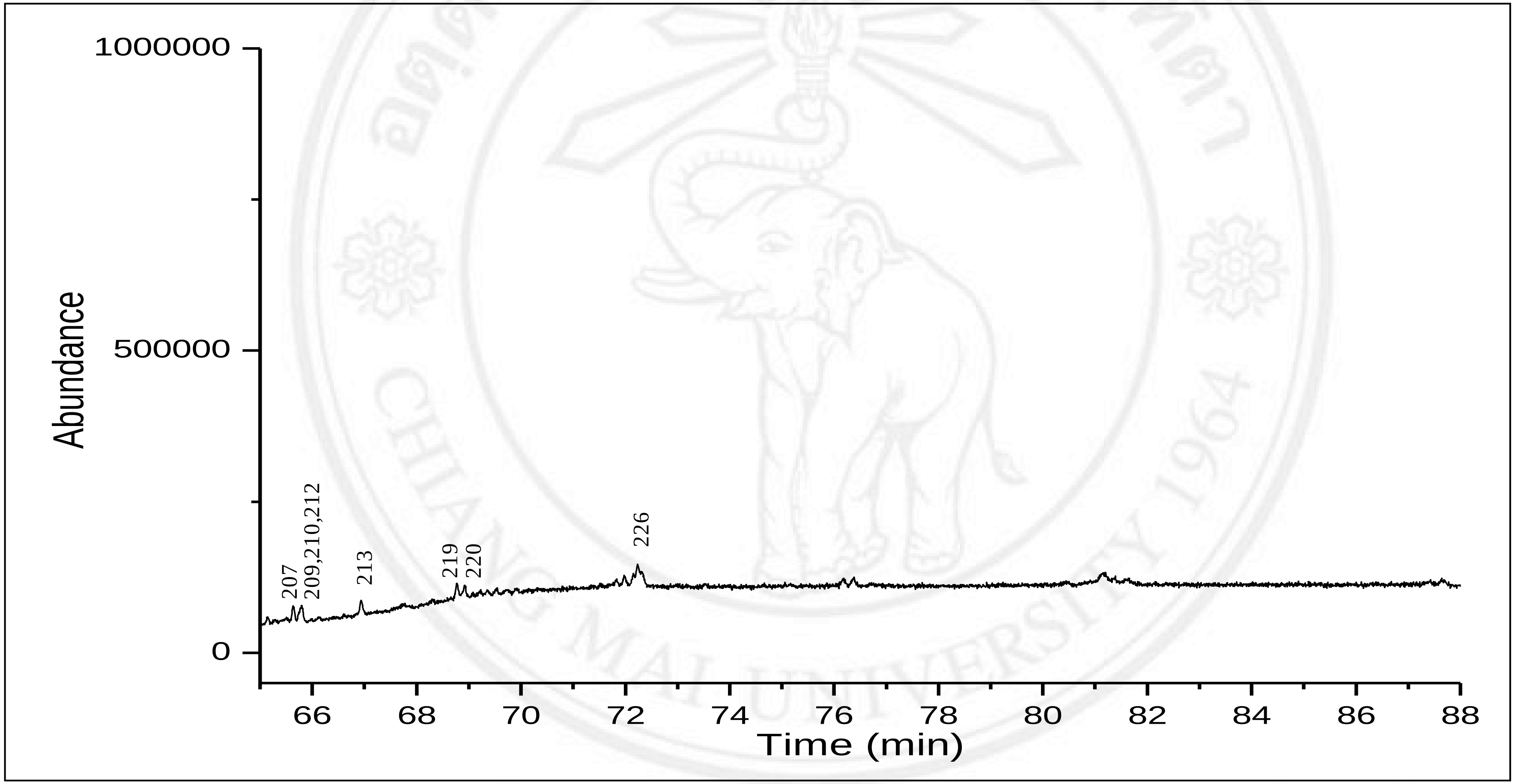

Figure 3.27 GC-MS chromatogram of top layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min (continued)

The GC-MS chromatogram of the bio-oil pyrolyzed at temperature of 600 °C and heating rate of 50 °C/min is presented in Figure 3.27. The results are similarly to the bio-oil obtained at temperatures 400 °C and 500 °C. The bio-oil components obtained from pyrolysis temperatures of 400 °C, 500 °C and 600 °C were compared.

Obviously, 2,5-dimethylpyridine and (1,3-dimethylbutyl)benzene, were found only in this sample, not in other top layer samples. At heating rate 50 °C/min, the organic components such as 2-methyl-2-pentanol, 3-methyl-3-pentanol, 5-hexen-2-one, 2-methylcyclopentanone, cyclohexanol and 2,4,6-trimethylpyridine were found only at 600 °C but not found at temperatures 400 °C and 500 °C. Moreover, the contents of phenolics and *N*-,*O*-heterocyclic derivatives obtained at this pyrolysis process were higher than those found in the other top layer samples.

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
1	2-Methyl-2-Pentanol	a	$C_6H_{14}O$	702	0.956					1.016
2	3-Methyl-3-Pentanol	a	$C_6H_{14}O$	729	0.505					0.812
3	5-Hexen-2-one	a	$C_6H_{10}O$	751	0.590					0.545
4	2-Hexanone	a	$C_6H_{12}O$	762	1.940	0.115	0.093	0.081		2.275
5	2-Hexanol	b	$C_6H_{14}O$	800	1.881	0.128	0.126	0.089		2.421
6	2-Methylpyridine	b	C_6H_7N	806		0.084	0.085	0.096		0.043
7	2-Methylcyclopentanone	a	$C_6H_{10}O$	832	0.721					0.748
8	3-Methylcyclopentanol	a	$C_6H_{12}O$	843	0.133			0.118		
9	2-Furanmethanol	b	$C_5H_6O_2$	849	0.465	0.065	0.049		0.662	0.582
10	Ethylbenzene	b	C_8H_{10}	857	0.407	0.090	0.070	0.046		0.609
11	1,2-Dimethylpyridine	b	$C_7H_{11}N$	860				0.090		0.045
12	2,6-Dimethylpyridine	b	C_6H_9N	881	0.185		0.052	0.044		0.048
13	Cyclohexanol	a	$C_6H_{12}O$	900	1.441					0.207
14	2,3-Dimethylpyridine	b	C_7H_9N	902	0.261	0.249	0.081	1.314	0.128	0.028
15	3,5-Dimethylpyridine	a	C_7H_9N	924	0.881		0.204	0.023		2.002
16	2,4-Dimethylpyridine	b	C_7H_9N	931					0.127	0.088
17	2-Cyclohexen-1-one	a	C_6H_8O	935	0.255			0.163	0.219	0.313
18	2,5-Dimethylpyridine	a	C_7H_9N	941						0.069
19	Unknown	a			0.318			0.272	0.301	0.406
20	Propylbenzene	b	C_9H_{12}	969		0.111		0.066	0.044	0.569

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
21	Unknown	a			0.174	0.263	0.219	0.135	0.175	0.086
22	Unknown	a			0.982	0.841	0.370	0.188	0.081	0.667
23	Unknown	a				0.112	0.281	0.178	1.059	0.275
24	Phenol	b	C_6H_6O	988	2.904	3.669	5.032	4.696	4.755	6.176
25	2,4,6-Trimethylpyridine	b	$C_8H_{11}N$	998	3.708		0.122			0.120
26	Unknown	a			0.176	0.180	0.219	0.040		0.063
27	Trimethylpyrazine	a	$C_7H_{10}N_2$	1002	0.296		0.077	0.116	0.104	0.078
28	2-Ethyl-6-methylpyrazine	b	$C_7H_{10}N_2$	1008	0.117			0.091		0.105
29	1-Ethenyl-2(1H)-pyridinone	a	C_7H_7NO	1012		0.118	0.120	0.167	0.097	0.056
30	2-Ethyl-6-methylpyridine	a	$C_8H_{11}N$	1019		0.130		0.090	0.057	0.056
31	Unknown	a				0.144	0.214	0.138	0.137	0.161
32	1-Ethynyl-2-methylbenzene	a	C_9H_8	1038					0.091	
33	(1-Methylpropyl)benzene	a	$C_{10}H_{14}$	1046				0.084		0.063
34	2,3-Dimethyl-2-cyclopenten-1-one	b	$C_7H_{10}O$	1048	0.454	0.333	0.276	0.247	0.127	0.329
35	Unknown	a				0.117		0.083		
36	Unknown	a				0.140	0.158	0.190	0.177	0.072
37	2-Methylphenol	b	C_7H_8O	1065	1.225	1.291	1.336	1.325	1.072	0.125
38	Acetophenone	a	C_8H_8O	1067	0.064	0.075	0.162	0.854	1.107	1.547
39	1-(1H-pyrrol-2-yl)ethanone	b	C_6H_7NO	1069	0.362	0.138	0.149	0.077		0.065
40	1-Octanol	a	$C_8H_{18}O$	1073	0.450	0.257	0.397	0.226	0.288	0.275

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
41	Unknown	a			0.159	0.333		0.095		0.055
42	3-Ethyl-2-cyclopenten-1-one	a	$C_7H_{10}O$	1077		0.295	0.094	0.426	0.235	0.299
43	1-Methyl-3-(1-methylethyl)benzene	a	$C_{10}H_{14}$	1078	0.149	0.131				0.092
44	Unknown	a				0.099				
45	Octanenitrile	a	$C_8H_{15}N$	1085	0.448	0.192	0.156	0.143	0.164	0.195
46	Unknown	a			0.106	0.256	0.290	0.102	0.178	0.211
47	4-Methylphenol	b	C_7H_8O	1087	2.372	3.565	4.360	3.707	4.391	4.685
48	1-Undecene	a	$C_{11}H_{22}$	1090		0.339	0.245	0.085		0.059
49	Unknown	a			0.153	0.333	0.441	0.106	0.124	0.069
50	(E)-Cinnamaldehyde	a	C_9H_8O	1096	0.298	0.188	0.067	0.066		0.194
51	2-Methylbenzofuran	a	C_9H_8O	1098	0.411	0.123	0.089	0.226	0.123	0.067
52	2,3-Cyclopentenopyridine	a	C_8H_9N	1100	0.507	0.215	0.183	0.251		0.077
53	Unknown	a				0.204	0.306			0.094
54	2-Methoxyphenol	b	$C_7H_8O_2$	1102	0.777	0.459	0.280	1.023	1.006	0.902
55	(2-Methyl-2-propenyl)benzene	a	$C_{10}H_{12}$	1111	0.104	0.208	0.106	0.146	0.122	0.125
56	2-Ethylidenecyclohexanone	a	$C_8H_{12}O$	1115	0.130	0.061		0.121	0.103	0.163
57	Unknown	a			0.181				0.175	0.164
58	Unknown	a			0.263	0.341	0.477	0.222		0.072
59	Unknown	a				0.185		0.068		0.253
60	(E)-1-Butenylbenzene	a	$C_{10}H_{12}$	1136	0.276	0.229	0.230	0.193		0.081

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
61	Unknown	a			0.161	0.241		0.088	0.113	0.082
62	1-Ethyl-2,5-pyrrolidinedione	a	$C_6H_9NO_2$	1145	0.249	0.154	0.179	0.167	0.125	0.190
63	2-Ethylphenol	b	$C_8H_{10}O$	1147		0.337	0.440	0.268	0.386	0.403
64	Unknown	a			0.331	0.490	0.624	0.333	0.385	0.398
65	Benzyl nitrile	a	C_8H_7N	1151	0.278	0.466	0.329	0.223	0.327	0.182
66	2,4-Dimethylphenol	b	$C_8H_{10}O$	1158	0.836	1.366	1.400	0.914	0.975	1.287
67	2,5-Dimethylphenol	b	$C_8H_{10}O$	1168	0.181	0.261	0.261	0.206	0.284	0.314
68	Unknown	a			0.249	0.449		0.251		0.171
69	2-Methyl-1H-indene	a	C10H10	1170	0.213	0.331	0.343	0.350	0.471	0.503
70	Pentylbenzene	a	C11H16	1172	0.187	0.250	0.553	0.468	0.632	0.269
71	1-Phenyl-1-propanone	b	$C_9H_{10}O$	1174	0.087	0.063	0.411	0.221	0.267	0.359
72	Unknown	a			0.164	0.221	0.224	0.147		0.184
73	Unknown	a			0.157	0.201	0.216	0.140		0.161
74	4-Ethylphenol	b	$C_8H_{10}O$	1177	2.184	2.635	3.152	2.234	2.354	2.640
75	3,4-Dimethylphenol	b	$C_8H_{10}O$	1181	0.183	0.193	0.191	0.275	0.477	0.539
76	3-Ethylphenol	a	$C_8H_{10}O$	1182		0.129	0.161	0.100	0.181	0.186
77	1-Decene	b	$C_{10}H_{20}$	1183	0.418	0.253	0.190	0.434	0.407	0.227
78	Unknown	a			0.193	0.290	0.500	0.121	0.198	0.250
79	Dodecane	b	$C_{12}H_{26}$	1200	0.416	0.260	0.145	0.416	0.260	0.145
80	1-Heptyl-2-methylcyclopropane	a	$C_{11}H_{22}$	1201	0.163	0.149		0.069		

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
81	Unknown	a				0.196		0.123	0.231	0.197
82	2-Methoxy-4-methylphenol	b	$C_8H_{10}O_2$	1202	0.159		0.125	0.259	0.233	0.198
83	4,7-Dimethylbenzofuran	a	$C_{10}H_{10}O$	1207	0.436	0.425	0.149	0.403	0.267	0.176
84	Naphthalene	b	$C_{10}H_8$		0.450	0.431	0.795	0.492	0.634	0.625
85	Isoquinoline	a	C_9H_7N	1233	0.299	0.137	0.199	0.028	0.092	0.207
86	2-Ethyl-6-methylphenol	a	$C_9H_{12}O$	1235					0.067	
87	3,5-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine	b	$C_9H_{12}N_2$	1236	0.306	0.177		0.340	0.226	0.172
88	(1,3-Dimethylbutyl)benzene	a	$C_{12}H_{18}$	1248						0.124
89	3-Ethyl-6-methylphenol	b	$C_9H_{12}O$	1260	0.306	0.457	0.603	0.526	0.727	0.811
90	1-Ethyl-4-methoxybenzene	a	$C_9H_{12}O$	1262	0.371	0.447	0.411	0.358	0.782	0.412
91	Benzenepropanenitrile	b	C_9H_9N	1263	0.768	0.882	0.565	0.959	0.683	0.525
92	Unknown	b						0.143	0.288	0.161
93	2,3-Dihydro-1,6-dimethyl-1H-indene	a	$C_{11}H_{14}$	1269		0.169		0.065	0.169	0.244
94	2,3-Dihydro-1H-inden-1-one	b	C_9H_8O	1269	0.632		0.189	0.219	0.286	0.311
95	Unknown	a				0.240	0.518	0.168		0.156
96	Unknown	a			0.309	0.480	0.747	0.403	0.444	0.372
97	Unknown	a						0.195	0.507	0.274
98	Unknown	a			0.424	0.487		0.324	0.258	0.385
99	Unknown	a			0.203	0.461	0.749	0.349	0.174	0.226
100	1-Tridecene	b	$C_{13}H_{26}$	1286	1.078	0.794	0.498	1.257	0.773	0.731

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
101	4-Ethyl-2-methoxyphenol	b	$C_9H_{19}O_2$	1295	0.611	0.371	0.277	0.611	0.371	0.277
102	Unknown	a			0.363	0.563	0.631	0.670	0.876	0.944
103	Tridecane	b	$C_{13}H_{28}$	1300	0.914	0.669	0.384	1.646	1.103	0.659
104	3,7-Dimethyl-1-octene	a	$C_{10}H_{20}$	1307		0.187	0.306	0.164		0.134
105	Unknown	a				0.117	0.299	0.170	0.054	0.134
106	1-Ethylidene-1H-indene	a	$C_{11}H_{10}$	1319		0.211	0.245	0.266	0.268	0.421
107	Heptylbenzene	a	$C_{13}H_{20}$	1307	0.146	0.227	0.420	0.307	0.335	0.443
108	1-Methyl-2-n-hexylbenzene	a	$C_{13}H_{20}$	1331	0.404			0.011		0.182
109	1H-Indole	b	C_8H_7N	1331		0.846	0.755			
110	1,2,3-Trimethylindene	a	$C_{12}H_{14}$	1331	0.330	0.344	0.353	0.333	0.429	0.456
111	1-Methylnaphthalene	b	$C_{11}H_{10}$	1321	0.523	0.535	0.852	0.667	0.723	0.731
112	Unknown	a						0.152	0.245	
113	2-Methylnaphthalene	a	$C_{11}H_{10}$	1379	0.342	0.462	0.616	0.488	0.584	0.644
114	1,1,3-Trimethyl-1H-indene	a	$C_{12}H_{14}$	1380	0.246	0.307	0.375	0.305	0.300	0.702
115	Unknown	a				0.143	0.301	0.302	0.304	0.238
116	2,6-Dimethoxyphenol	b	$C_8H_{10}O_3$	1381		0.339	0.277	0.420	0.385	0.229
117	Unknown	a			0.211	0.328	0.736	0.655	0.297	0.391
118	Unknown	a				0.329	0.560	0.520	0.413	0.258
119	2-Butyl-2-octenal	b	$C_{12}H_{22}O$	1386	1.211	3.116	3.834	3.944	5.949	1.009
120	Unknown	a			0.198	0.376		0.397	0.067	0.188

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
121	1-Tetradecene	b	$C_{14}H_{28}$	1388	1.313	1.062	0.415	1.432	1.317	0.965
122	2-Ethylnaphthalene	b	$C_{12}H_{12}$	1398		0.116			0.100	0.274
123	Diphenylmethane	a	$C_{13}H_{12}$	1399	0.163	0.302	0.482	0.303	0.410	0.439
124	Tetradecane	a	$C_{14}H_{30}$	1400	1.233	1.205	1.037	1.731	1.393	1.068
125	Unknown	a			0.146	0.195		0.214	0.191	0.318
126	(Z)-5-Tetradecene	a	$C_{14}H_{28}$	1409	0.141	0.293	0.355	0.211	0.282	0.380
127	1,8-Dimethylnaphthalene	b	$C_{12}H_{12}$	1414	0.230	0.344	0.337	0.213	0.297	0.321
128	Unknown	a				0.171	0.262	0.177		0.315
129	Unknown	a				0.268	0.402	0.189	0.286	0.347
130	4-Methyl-1H-indole	a	C_9H_9N	1435	0.740	0.715	0.323	0.731	0.668	0.525
131	Unknown	a						0.203		0.209
132	1,5-Dimethylnaphthalene	b	$C_{12}H_{12}$	1437		0.161	0.200	0.196	0.205	0.361
133	2,6-Dimethylnaphthalene	b	$C_{12}H_{12}$	1438	0.235	0.230	0.354	0.245	0.296	0.357
134	8-Phenyl-1-octanol	a	$C_{14}H_{22}O$	1451		0.202	0.520	0.334	0.350	0.453
135	2,3,5,8-Tetramethyldecane	a	$C_{14}H_{30}$	1465	0.925	0.623	0.410	0.759	0.797	0.884
136	(1-Methylheptyl)benzene	a	$C_{14}H_{22}$	1470			0.295	0.239	0.528	0.438
137	Octylbenzene	b	$C_{14}H_{22}$	1472	0.288	0.335	0.449	0.483	0.556	0.755
138	Unknown	a			0.236	0.352	0.442	0.612	0.180	
139	Unknown	a			0.208	0.434	0.667	0.384	0.218	
140	8-Dodecenol	a	$C_{12}H_{24}O$	1488	0.632	1.085	0.575	0.698	1.119	0.716

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
141	Unknown	a						0.032		0.113
142	1-Pentadecene	b	$C_{15}H_{30}$	1493	1.789	1.394	0.571	1.746	1.717	1.073
143	Unknown	a			0.286					0.181
144	Unknown	a								0.512
145	Pentadecane	b	$C_{15}H_{32}$	1500	2.361	1.610	1.376	2.227	1.751	1.436
146	(1-Methyldodecyl)benzene	a	$C_{19}H_{32}$	1503		0.280	0.328	0.275		0.292
147	2-(1-Methylethyl)naphthalene	a	$C_{13}H_{14}$	1505	0.362	0.529		0.232		0.573
148	Unknown	a			0.548					0.549
149	(Z)-3-Tetradecene	a	$C_{14}H_{28}$	1521		0.210	0.396	0.188	0.233	0.331
150	Unknown	a					0.326			
151	Unknown	a			0.224		0.316	0.321		
152	Unknown	a						0.222		0.127
153	Unknown	a			0.188	0.148		0.217	0.074	0.156
154	Unknown	a			0.161	0.107		0.261	0.231	0.226
155	Unknown	a			0.129	0.229		0.163		
156	1,12-Tridecadiene	a	$C_{13}H_{24}$	1554	0.430	0.382	0.206	0.411	0.298	0.242
157	Unknown	a			0.115	0.224	0.326	0.147	0.183	0.188
158	Nonylbenzene	b	$C_{15}H_{24}$	1564				0.129	0.167	0.192
159	Unknown	a			0.116	0.306	0.404	0.229	0.207	0.184
160	1,10-Undecadiene	a	$C_{11}H_{20}$	1585		0.544	0.498	0.909	0.404	0.363

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
161	1-Hexadecene	b	$C_{16}H_{32}$	1592	1.738	1.502	1.061	1.919	1.639	1.227
162	Fluorene	a	$C_{13}H_{10}$	1587		0.208		0.152	0.399	
163	Hexadecane	b	$C_{16}H_{34}$	1600	1.540	1.128	1.006	1.540	1.128	1.006
164	2-Methyldodecane	a	$C_{13}H_{28}$	1617	0.506	0.472	0.418	0.682	0.445	0.318
165	Unknown	a			0.292	0.424	0.809	0.265	0.290	0.366
166	Unknown	a						0.185		0.124
167	Unknown	a				0.169		0.185		
168	Unknown	a			0.211	0.304	0.541	0.139	0.202	0.227
169	Unknown	a			0.103	0.216	0.546	0.276		0.345
170	2,5,9-Trimethyldecane	a	$C_{13}H_{28}$	1592	0.766	0.354	0.338	0.876	0.685	0.463
171	1,11-Dodecadiene	a	$C_{12}H_{22}$	1597		0.100		0.401	0.135	
172	Allyl nonyl oxalate	a	$C_{14}H_{24}O_4$	1653		0.127	0.293	0.219	0.201	0.258
173	(E)-7-Tetradecene	a	$C_{14}H_{28}$	1683	1.041	0.913	0.508	1.164	0.891	0.513
174	1-Ethyl-2-heptylcyclopropane	a	$C_{12}H_{24}$	1689	0.586	0.440	0.277	0.604	0.532	0.400
175	1,13-Tetradecadiene	a	$C_{14}H_{26}$	1692	1.214	0.705	0.492		0.438	0.282
176	1-Heptadecene	b	$C_{17}H_{34}$	1683	1.598	0.943	0.064	1.898	1.553	1.156
177	Heptadecane	b	$C_{17}H_{36}$	1700	1.264	1.249	0.705	1.421	1.145	0.538
178	(1-Methyldecyl)benzene	a	$C_{17}H_{28}$	1709		0.299	0.620	0.367	0.465	0.502
179	6-Methyl-2-(4-methylpentyl)-1-heptene	a	$C_{14}H_{28}$	1734	1.851	1.818	1.753	1.991	1.849	1.392
180	Unknown	a			0.534	0.649	0.826	0.757	0.625	0.710

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
181	Unknown	a						0.314		0.116
182	Unknown	a			0.352	0.371	0.532	1.012	0.258	0.285
183	6,10-Dimethyl-2-undecanone	a	$C_{13}H_{26}O$	1780	1.273	0.862	0.528	0.629	0.514	0.489
184	Unknown	a			0.513	0.830	1.501	0.819	0.549	0.424
185	Unknown	a				0.512	0.703	0.426	0.628	0.728
186	1-Octadecyne	b	$C_{18}H_{34}$	1791		0.296		0.634	0.432	0.429
187	1-Octadecene	b	$C_{18}H_{36}$	1794	1.148	0.924	0.353	1.282	0.895	0.681
188	Octadecane	a	$C_{18}H_{38}$	1800		1.432	0.974	0.782	0.551	0.445
189	Unknown	a			0.314				0.526	0.605
190	Methyl tridecanoate	a	$C_{14}H_{28}O_2$	1807		0.268	0.495	0.294	0.216	0.341
191	9-Octadecenal	a	$C_{18}H_{34}O$	1821	0.871	0.402	0.309	1.009	0.651	0.338
192	Unknown	a								0.068
193	Unknown	a			0.491	0.662	1.000	0.694	0.646	0.375
194	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	a	$C_{20}H_{40}O$	1835	2.237	2.123	1.848	2.423	2.138	1.637
195	3,7,11,15-Tetramethyl-2-hexadecene	b	$C_{20}H_{40}$	1836	1.787	1.385	0.596		1.621	0.776
196	Methyl oleate	a	$C_{19}H_{36}O_2$	1842	0.372	0.471	0.805	0.488	0.574	1.678
197	Unknown	a			0.575	0.698	0.871	0.349	0.529	0.533
198	Caffeine	b	$C_8H_{10}N_4O_2$	1867	2.227	2.075	1.926	2.578	2.405	2.536
199	Unknown	a			0.127	0.457	1.393	2.130	1.776	1.783
200	Unknown	a			0.534	1.107	1.931	0.960	0.779	0.468

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
201	Unknown	a			0.599	0.990	1.300	1.607	1.386	0.688
202	Nonanamide	a	$C_9H_{19}NO$	1905	3.758					
203	Hexadecanenitrile	b	$C_{16}H_{31}N$	1911	0.504	1.147	2.773	0.999	1.055	1.298
204	Methyl hexadecanoate	b	$C_{17}H_{34}O_2$	1913	0.824	0.983	1.608	0.465	0.620	1.066
205	Unknown	a			0.247					
206	N-Methylvaleramide	a	$C_6H_{13}NO$	1921	0.406					
207	Unknown	a			0.252	0.533	0.880	0.384		0.595
208	Unknown	a			0.224	0.539				
209	Unknown	a			0.482	0.429		2.031	0.940	0.592
210	Unknown	a			0.615	0.921	1.853	0.946	0.863	0.936
211	2-Methyloctadecane	a	$C_{19}H_{40}$	2033	0.553	0.553			0.582	
212	Unknown	a			0.229	0.374	0.525		0.285	0.233
213	4-Methylcyclopentadecanone	a	$C_{16}H_{30}O$	2047	0.678	0.300	0.339	1.777	1.347	0.259
214	Allyl dodecyl oxalate	a	$C_{17}H_{30}O_4$	2067	0.415					
215	2-Methylnonadecane	a	$C_{20}H_{42}$	2079	0.773					
216	Unknown	a			0.216	0.397				
217	Unknown	a			0.323	0.623				
218	Unknown	a			0.255	0.391				
219	1-Docosene	a	$C_{22}H_{44}$	2107	1.635	1.115	0.725	0.924	0.167	0.617
220	Unknown	a			0.383	0.844	1.800	0.959	0.783	0.403

Table 3.1 Structural assignments of components in the top layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative contents					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
221	Unknown	a			0.348	1.218	1.890			
222	Unknown	a			0.183	0.290				
223	Unknown	a			0.216	0.475				
224	Allyl hexadecyl oxalate	a	$C_{21}H_{38}O_4$	2176		0.464			0.454	
225	Unknown	a			0.337	0.620				
226	Unknown	a			0.549	0.866	1.559	0.386	0.556	0.633
227	Unknown	a			0.183	0.375				
228	Unknown	a				0.343				
229	Allyl octadecyl oxalate	a	$C_{23}H_{42}O_4$	2244	0.369	0.419				
230	Heptacosane	a	$C_{27}H_{56}$	2247	0.629	0.515				
231	Unknown	a								0.228

a Found in GC×GC not GC

b Found in GC×GC and GC

By using GC×GC-TOF-MS, a number of additional components were detected which resulted in the total of at least 231 components found in the top layer bio-oil sample. Among these, 143 components were identified and classified in the groups of hydrocarbons, phenolics, aromatic compounds, ketones and aldehydes, esters, alcohols, *N*-, *O*-heterocyclic aromatic derivatives and nitrogenous compounds. The results showed that more than 62% of total chromatographic peaks could be identified with GC×GC-TOF-MS but only 52%, in the best case, with GC-MS.

Summation of the percentage peak areas of the identified components in all bio-oil samples from the top layer, compared with the total response of all peaks in the chromatogram are illustrated in Figure 3.28. The major groups of bio-oils in the top layer were hydrocarbons and phenolics compounds.

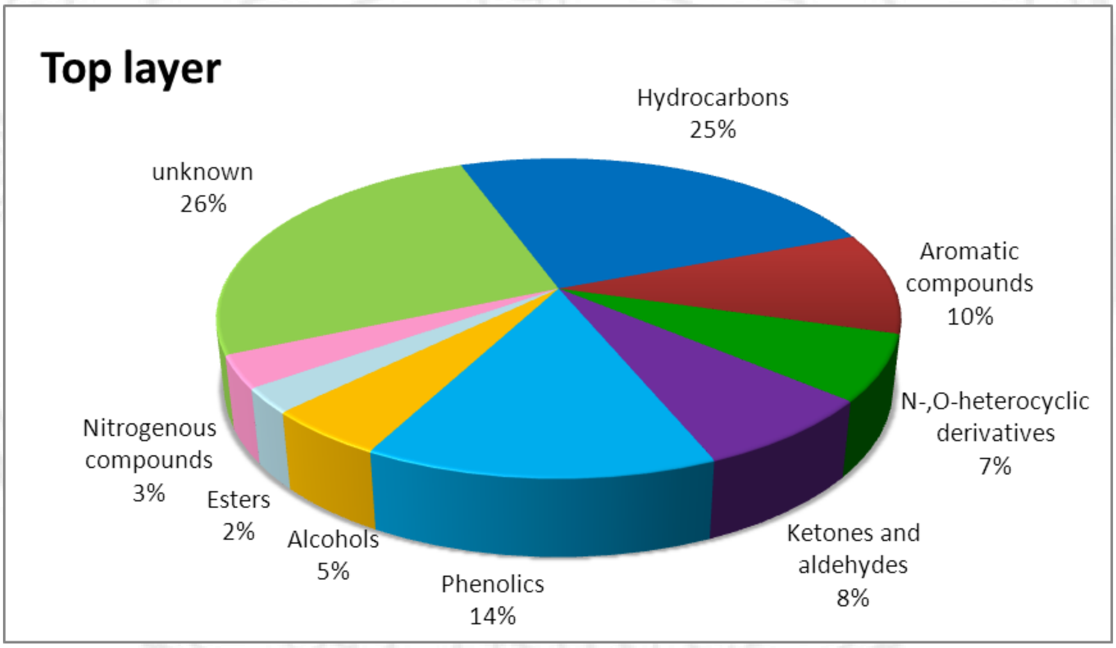

Figure 3.28 Comparison of percent relative amounts of each chemical group in the top layer of bio-oil samples

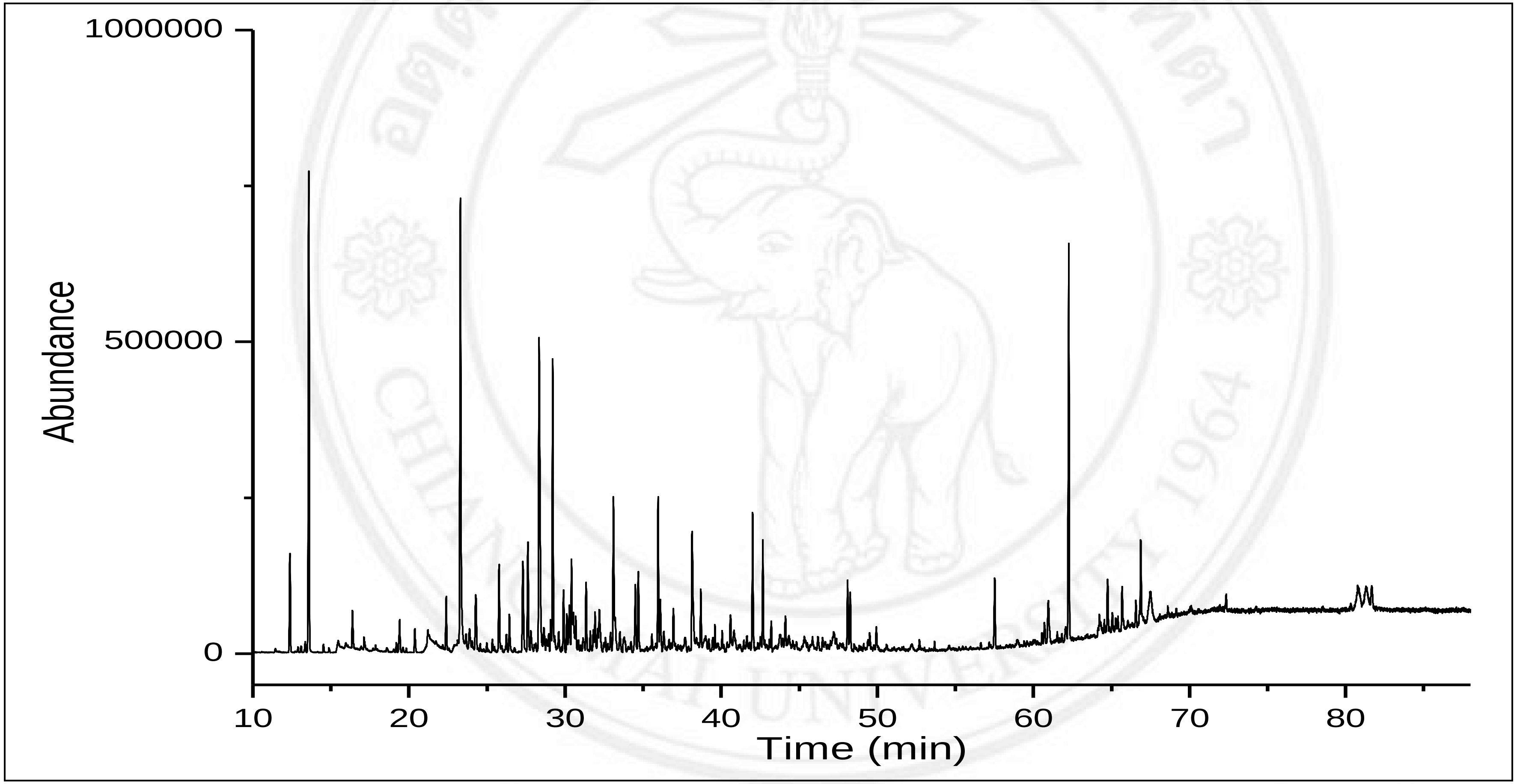

Figure 3.29 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min

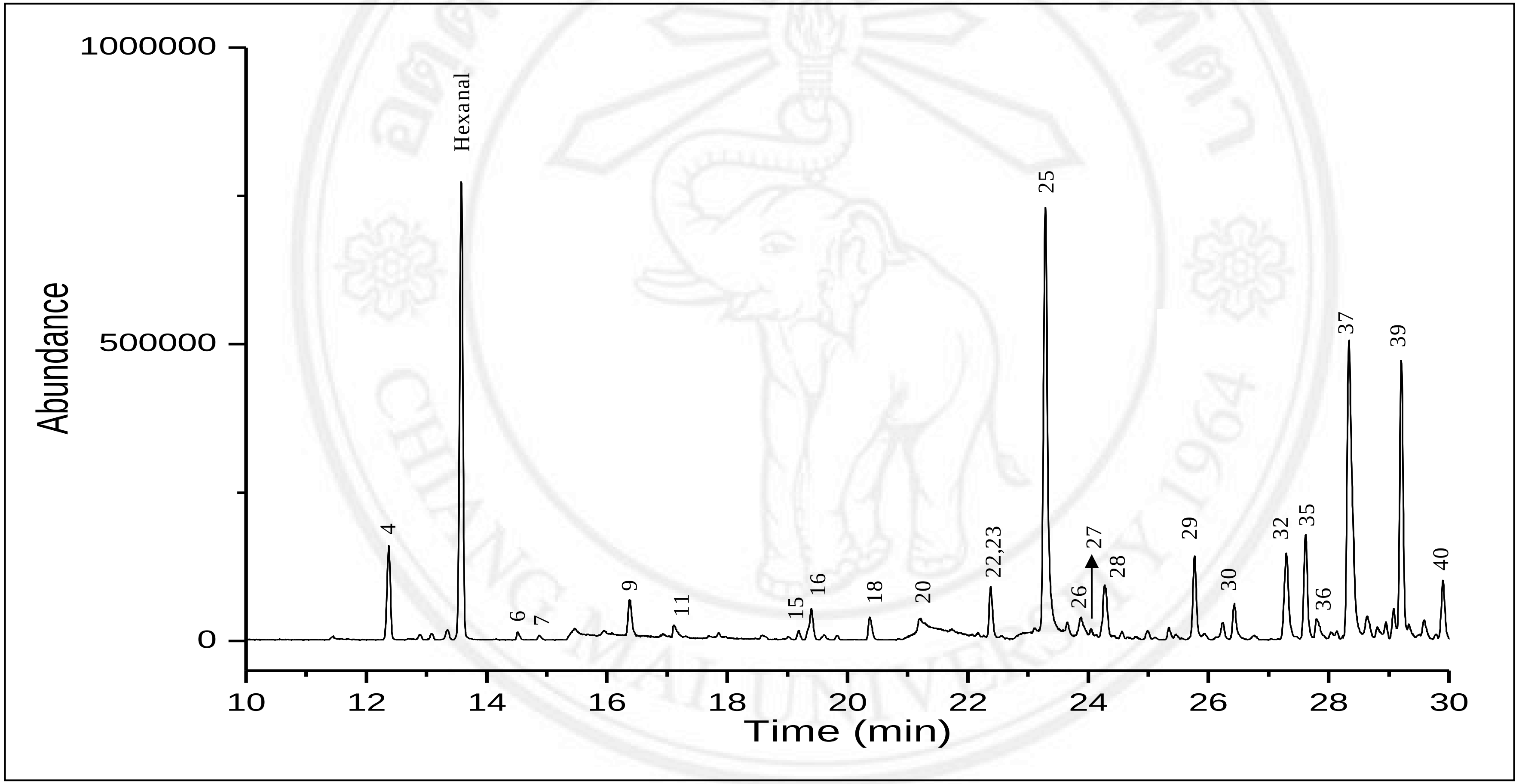

Figure 3.29 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued)

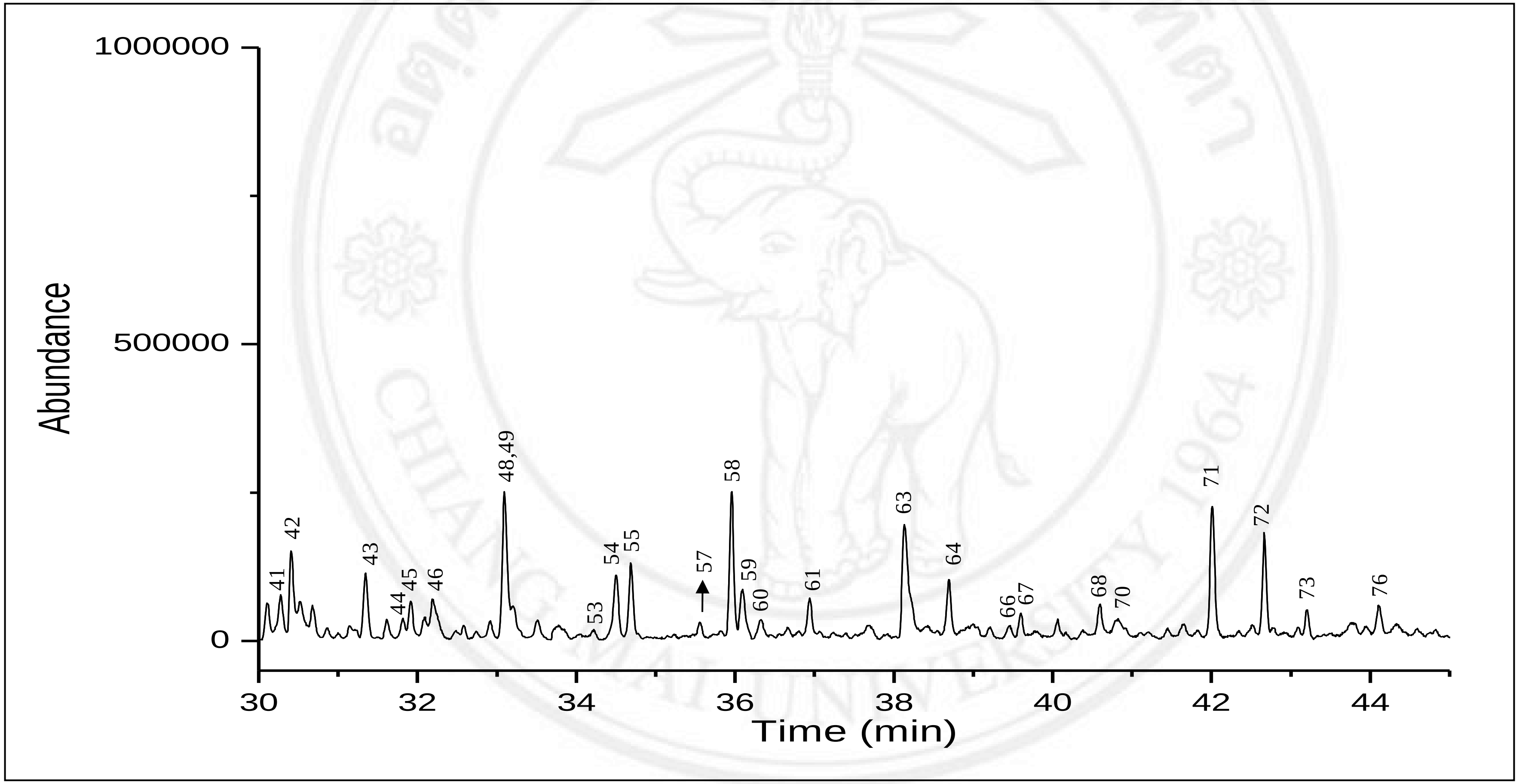

Figure 3.29 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued)

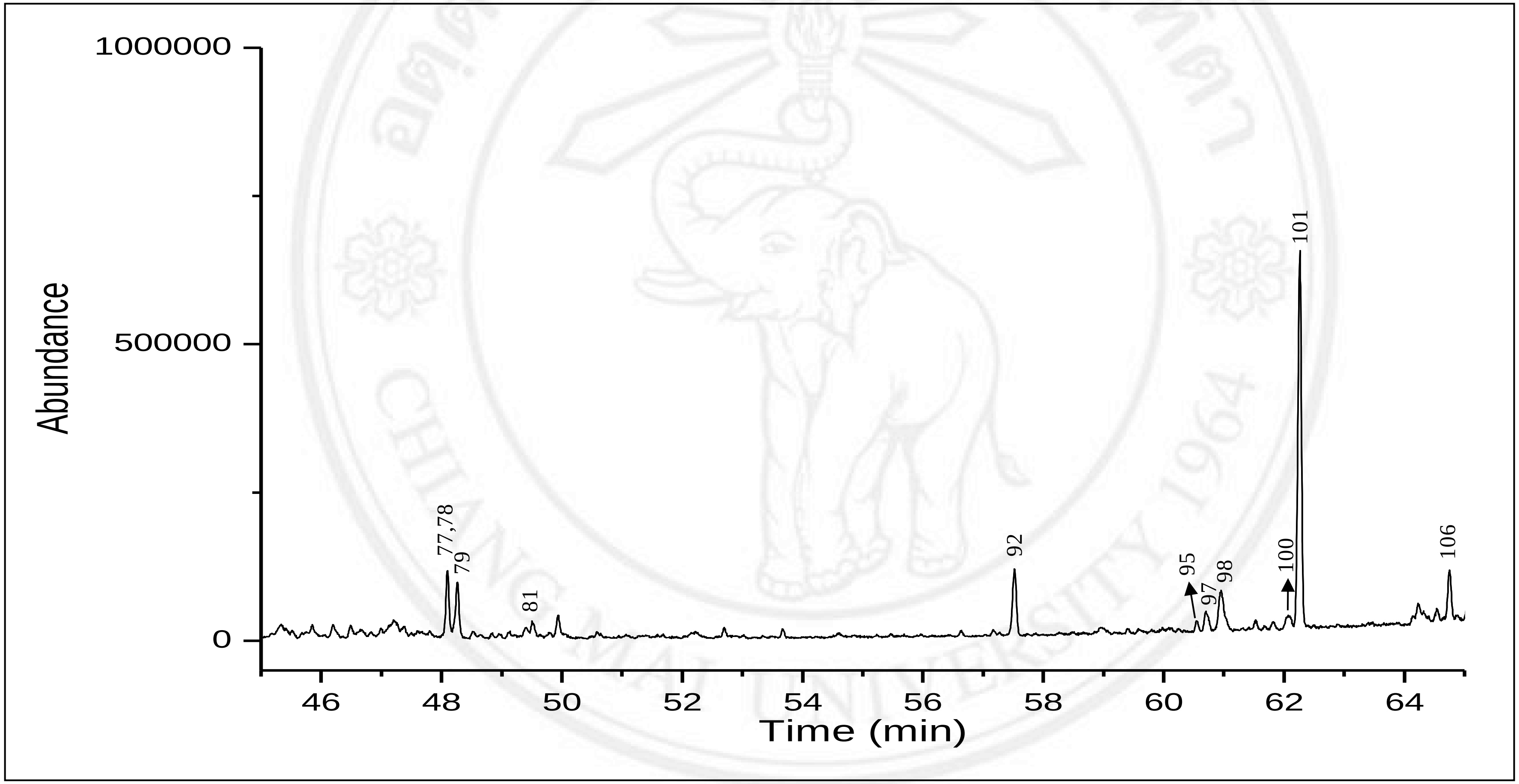

Figure 3.29 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued)

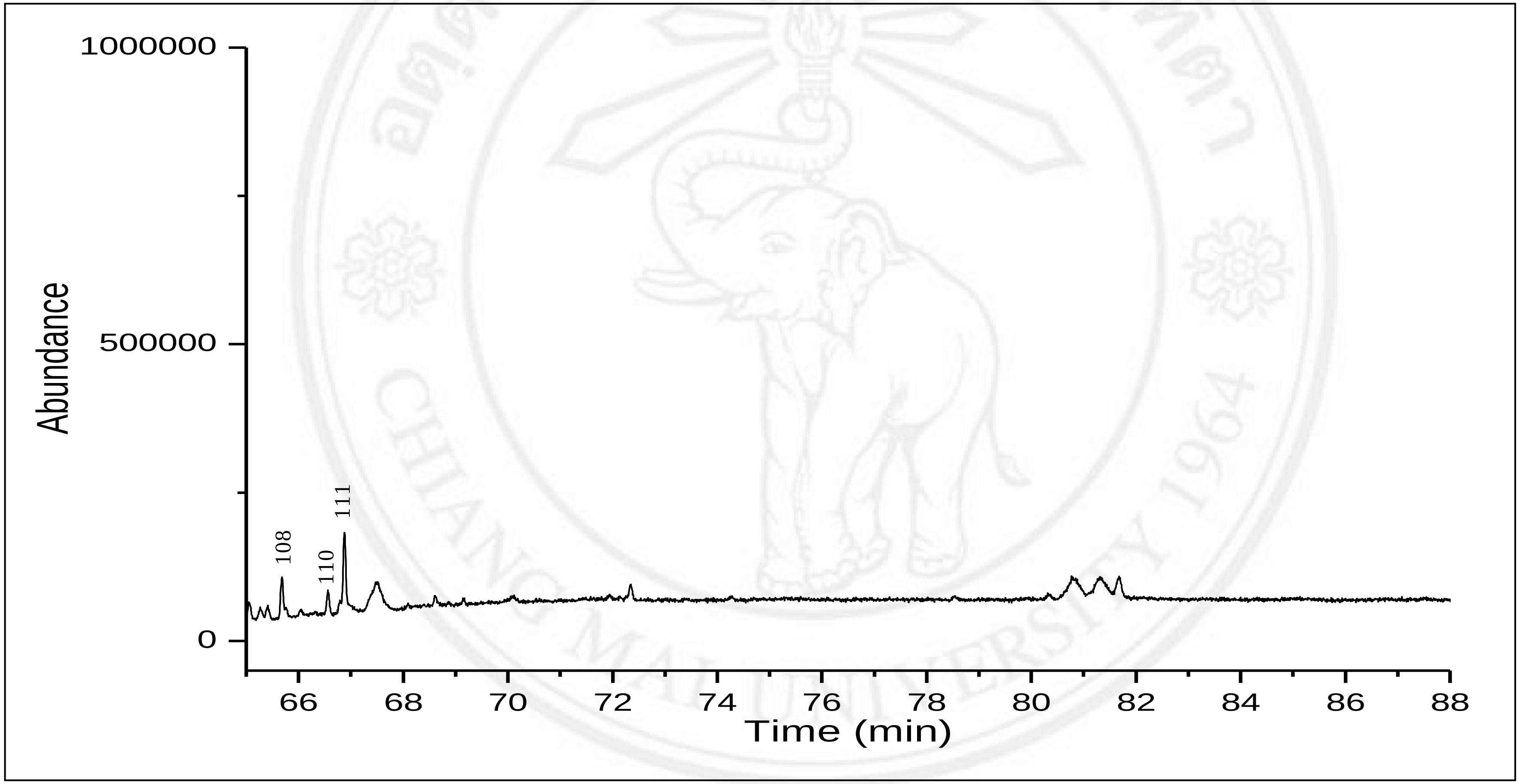

Figure 3.29 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 10 °C/min (continued)

For the bottom layer bio-oil, the components obtained from pyrolysis temperature of 400 °C and heating rate of 10 °C/min are shown in Figure 3.29. It can be seen that the contents of most organic components decreased especially in hydrocarbon groups. Hydrocarbons including 3,4-dimethyloctane, 1-tetradecene, 2,7,10-trimethyldodecane and 2-methyloctadecane, found in very low contents when compared with those in the top layer.

However, phenolics, including phenol, 4-methylphenol, 2-methoxyphenol, 4-methylphenol, were the major products of the bio-oil as same as the top layer bio-oil. The bio-oil components only found in this bottom layer sample, were 2-ethyl-3,5-dimethylpyridine and methyl hexadecanoate.

Additionally, some components which were not found in GC-MS chromatograms but showed in GC×GC contour plot, such as 2-hexanone, 4-hydroxy-4-methyl-2-pentanone, 1-(2-furanyl)ethanone, 3,5-dimethylpyridine, 2-cyclohexen-1-one, 1-ethynyl- 2-methylbenzene, 2-ethyl-3,5-dimethylpyridine, acetophenone, 1-octanol, 2-ethylidene cyclohexanone, 3,4-dimethyloctane, 1-phenyl-1-propanone, hexadecane nitrile, methyl hexadecanoate, 2-methyloctadecane and 4-methylcyclopentadecanone.

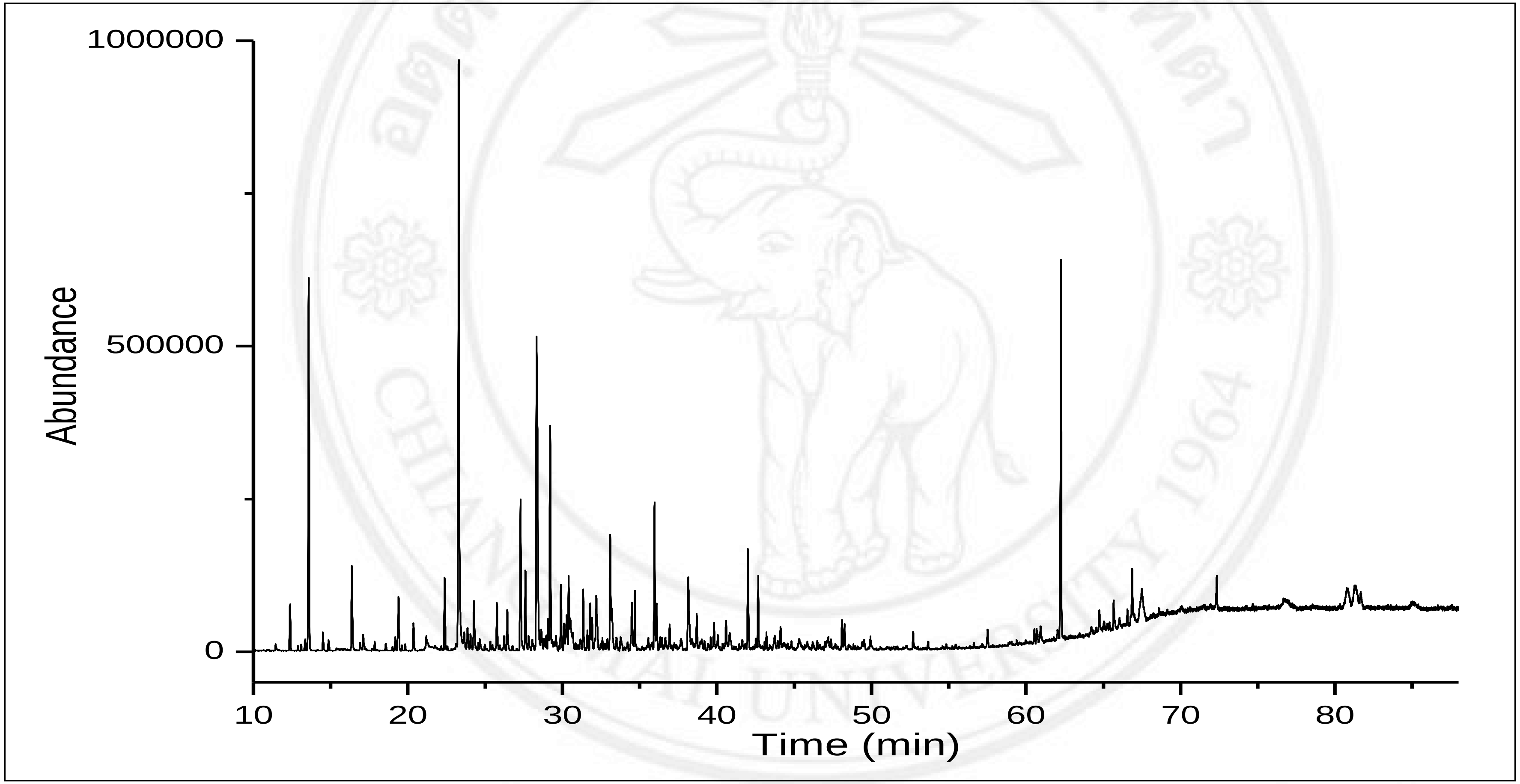

Figure 3.30 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min

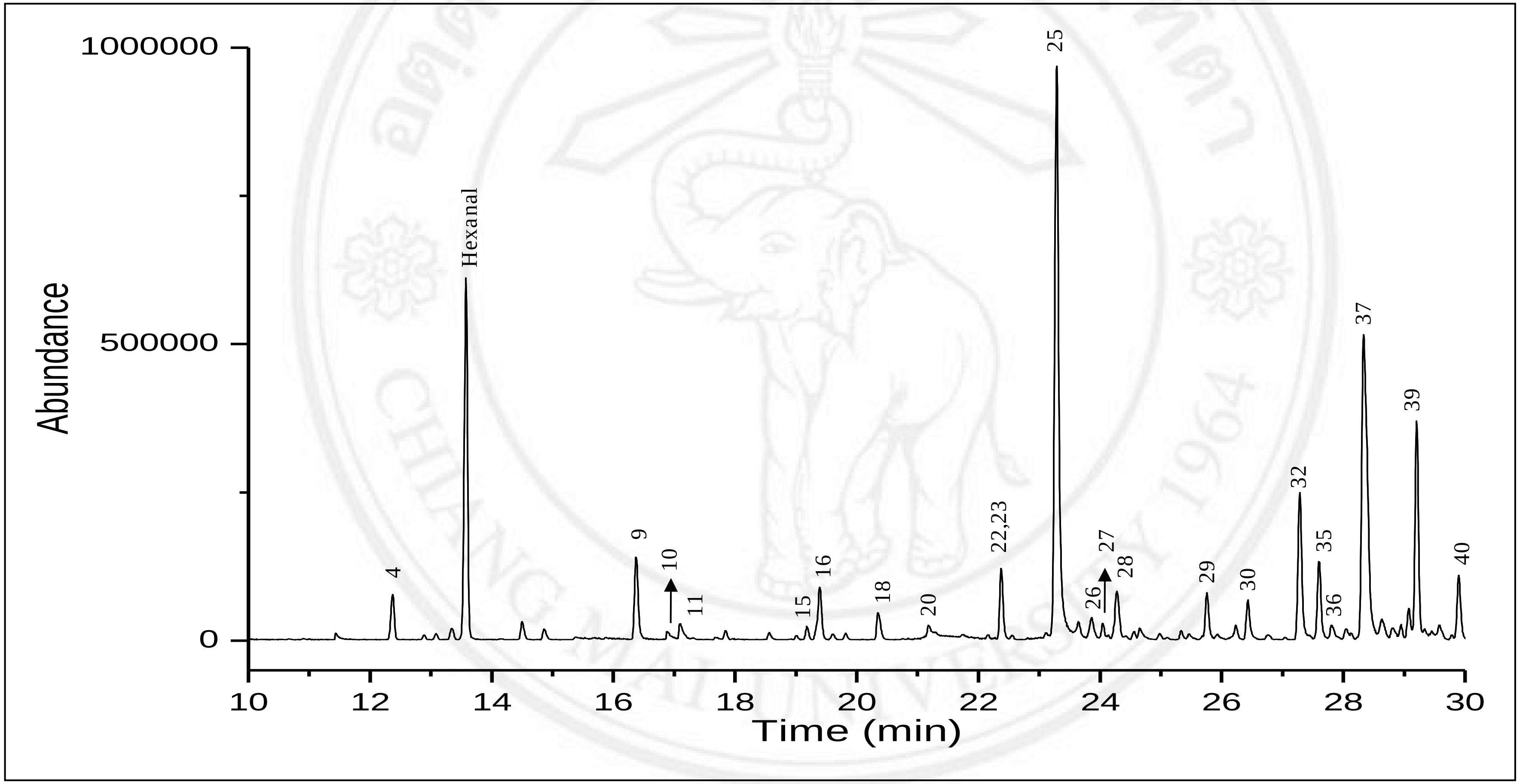

Figure 3.30 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

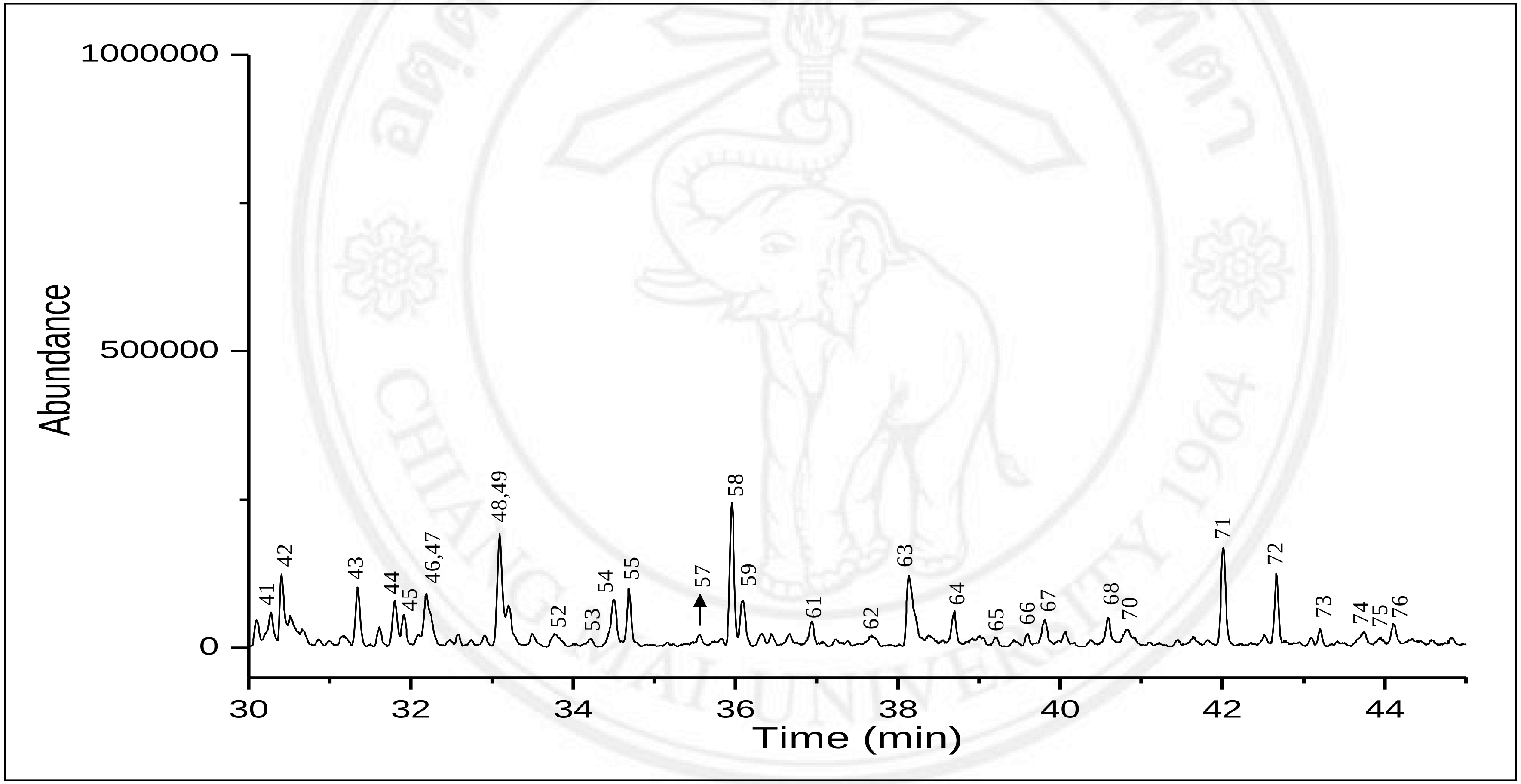

Figure 3.30 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

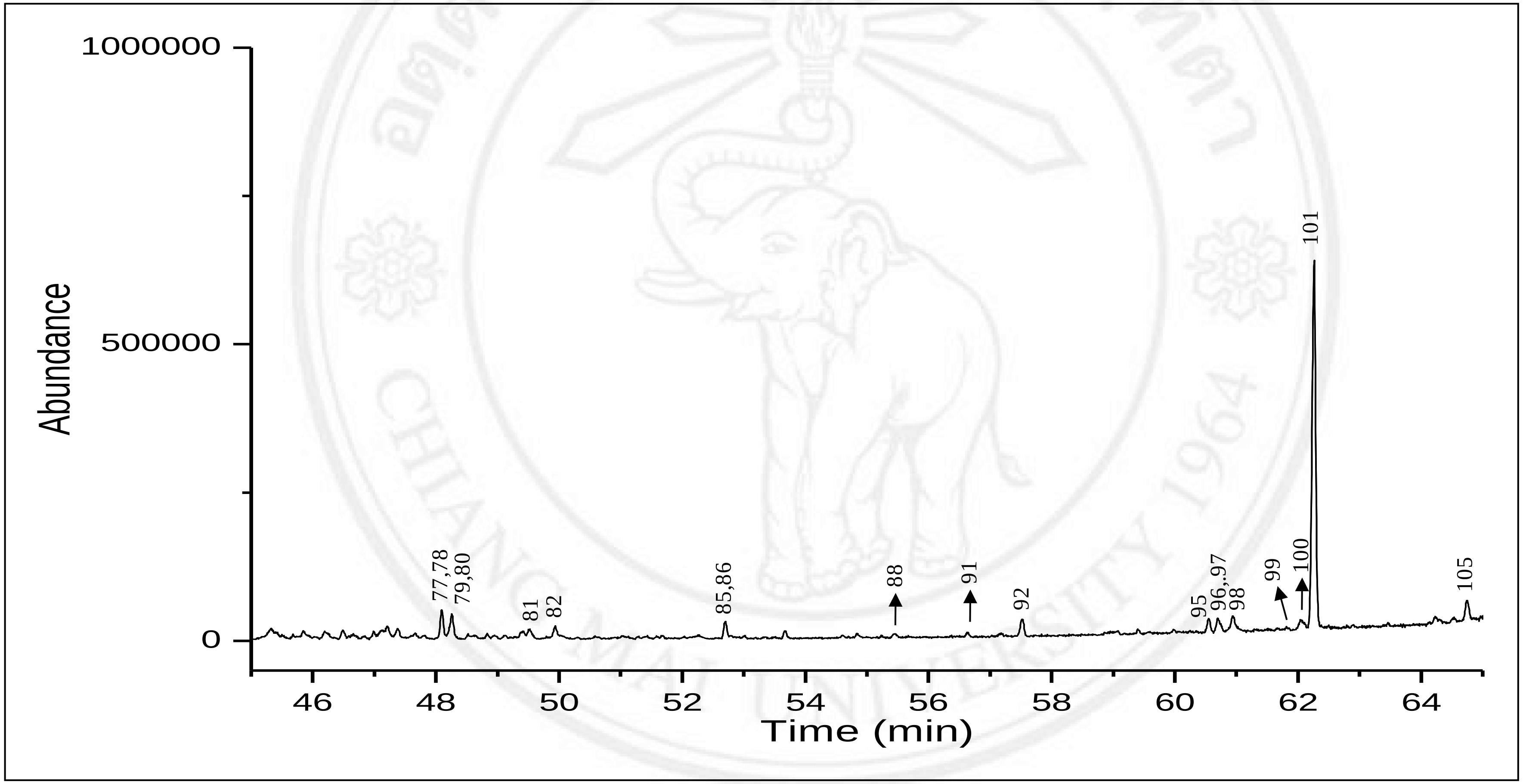

Figure 3.30 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

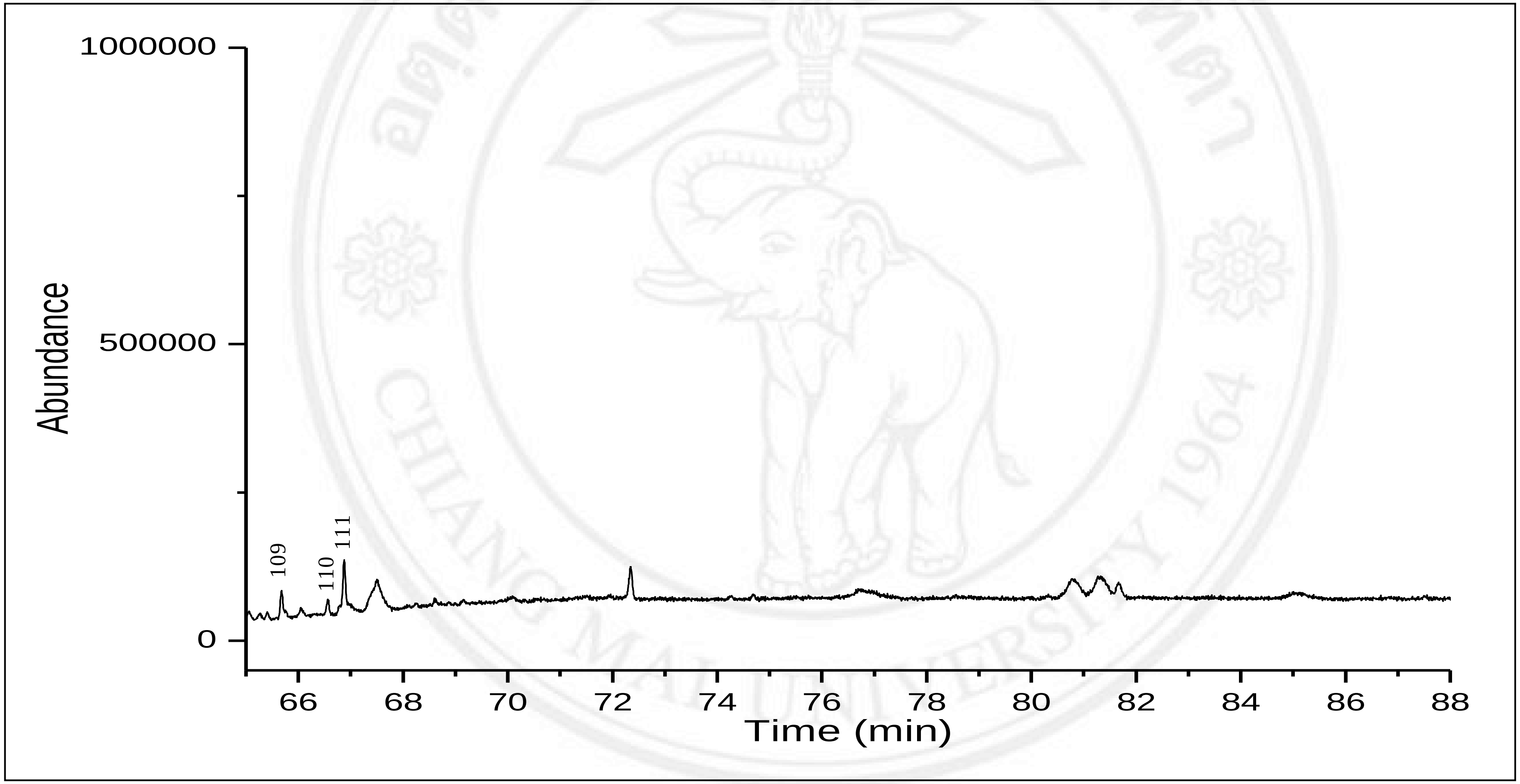

Figure 3.30 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 10 °C/min (continued)

Figure 3.30 shows the organic components of bottom layer bio-oil pyrolysed at pyrolysis temperature of 500 °C and heating rate of 10 °C/min. As can be seen in Table 3.2, some organic compounds including (Z)-3-tetradecene and nonylbenzene, were found only in the bio-oil obtained at 500 °C and heating rate of 10 °C/min.

In addition, ethylbenzene, acetophenone, 2,5-dimethylphenol, isoquinoline, heptylbenzen, tetradecane, (Z)-3-tetradecene, nonylbenzene, 2,5,9-trimethyldecane, 1,11-dodecadiene, 6-methyl-2-(4-methylpentyl)-1-heptene, undecanenitrile, 2-tetra decanone, methyl oleate, were found by GC×GC-TOF-MS, not by GC-MS.

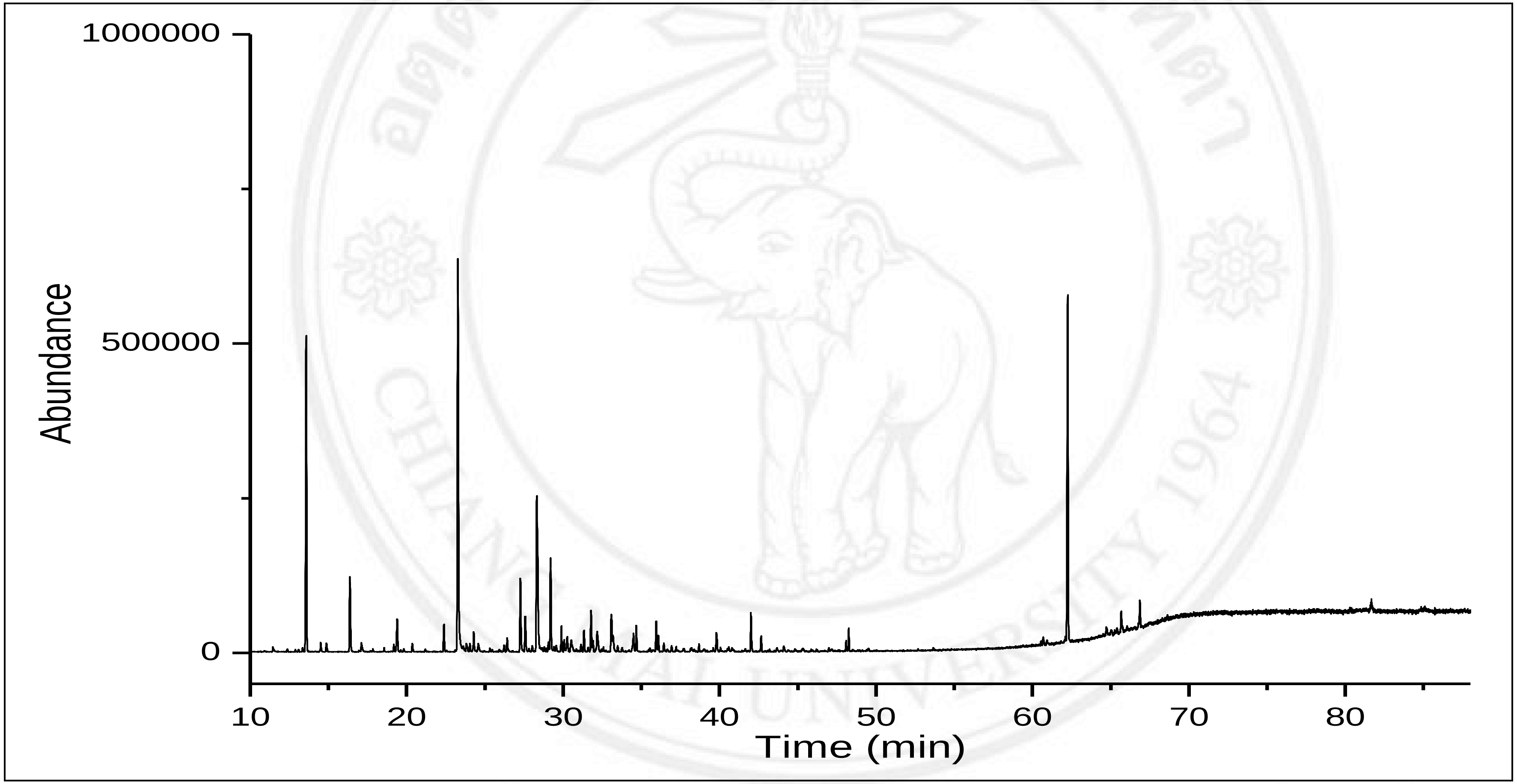

Figure 3.31 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min

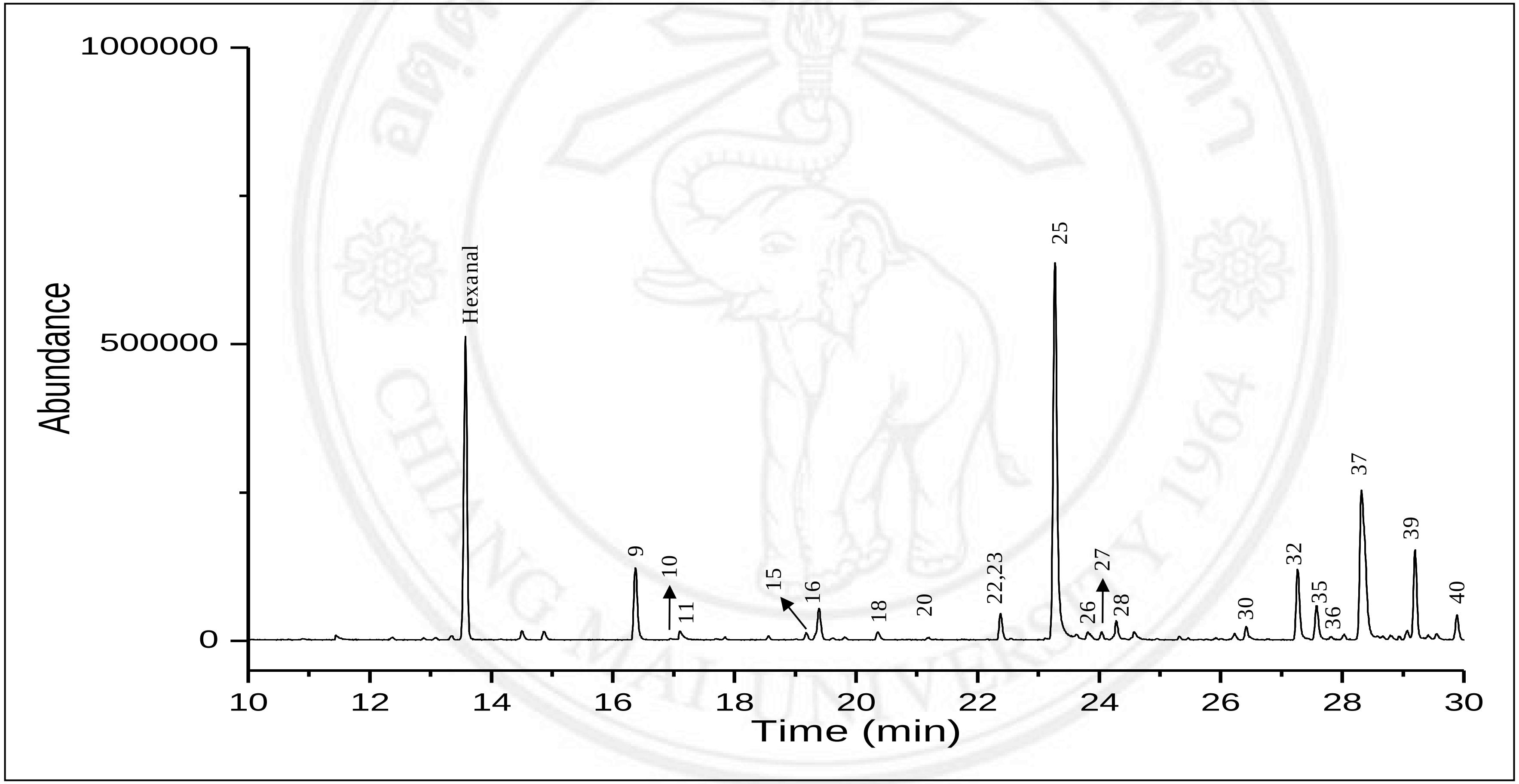

Figure 3.31 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min (continued)

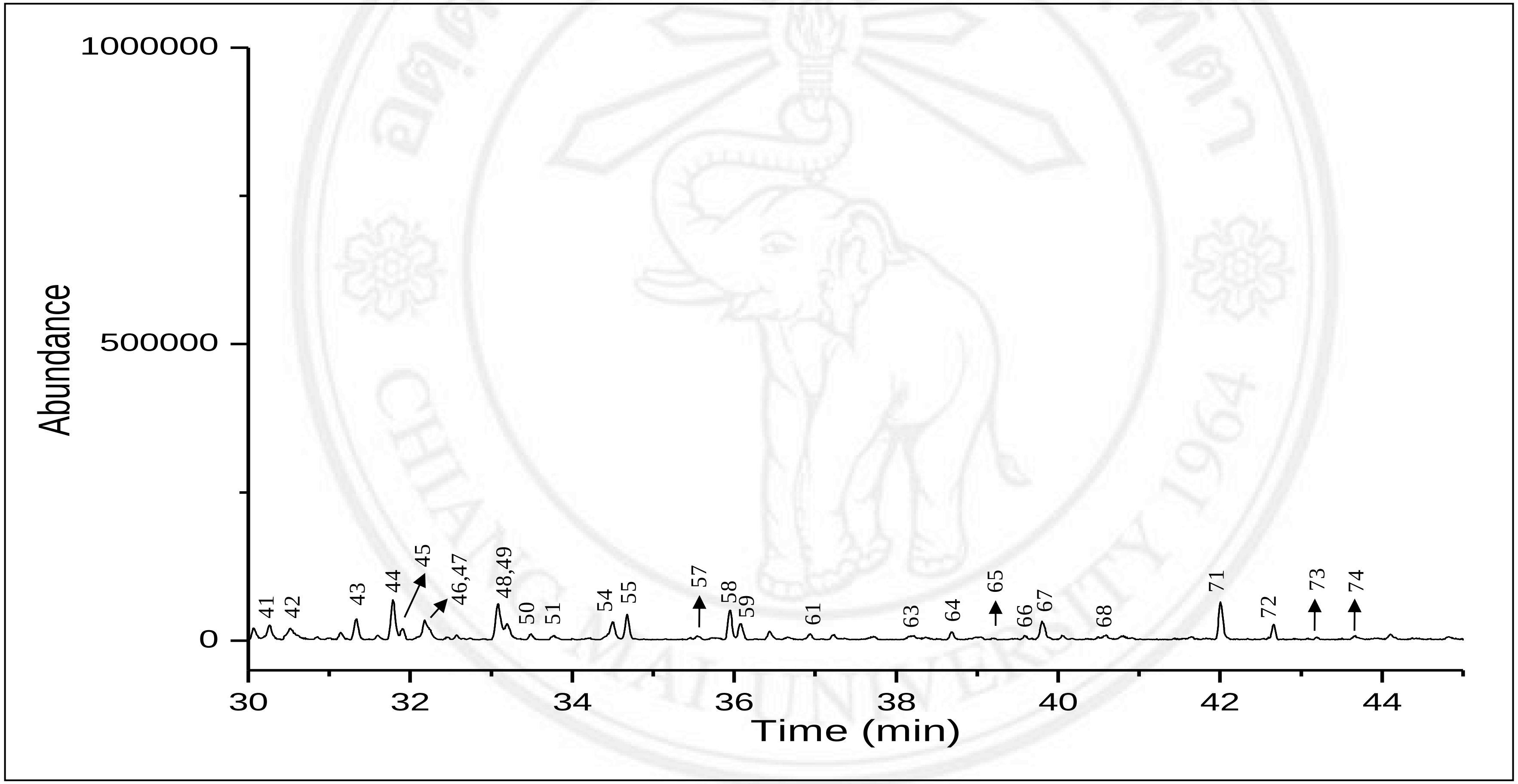

Figure 3.31 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate 10 °C/min (continued)

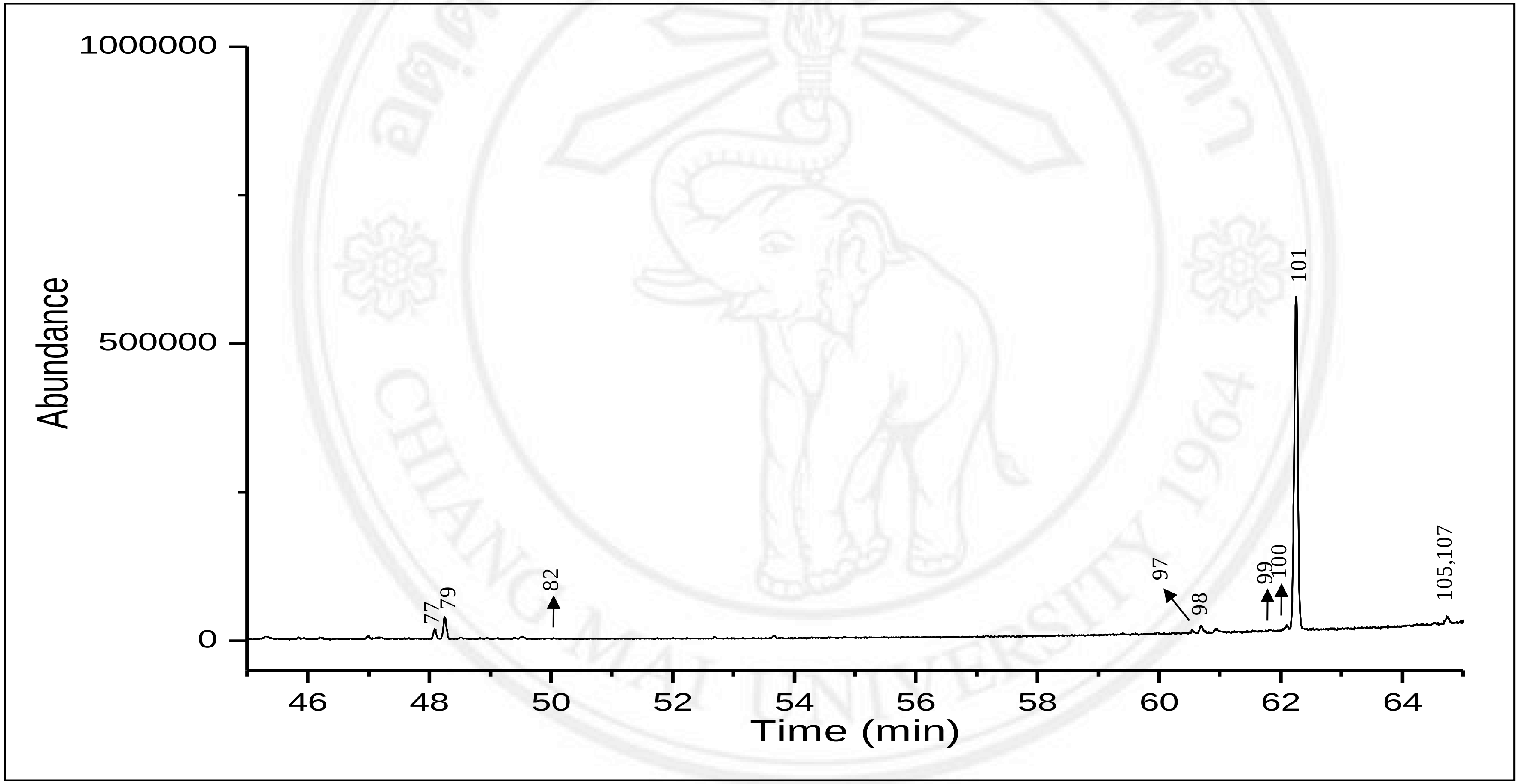

Figure 3.31 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min (continued)

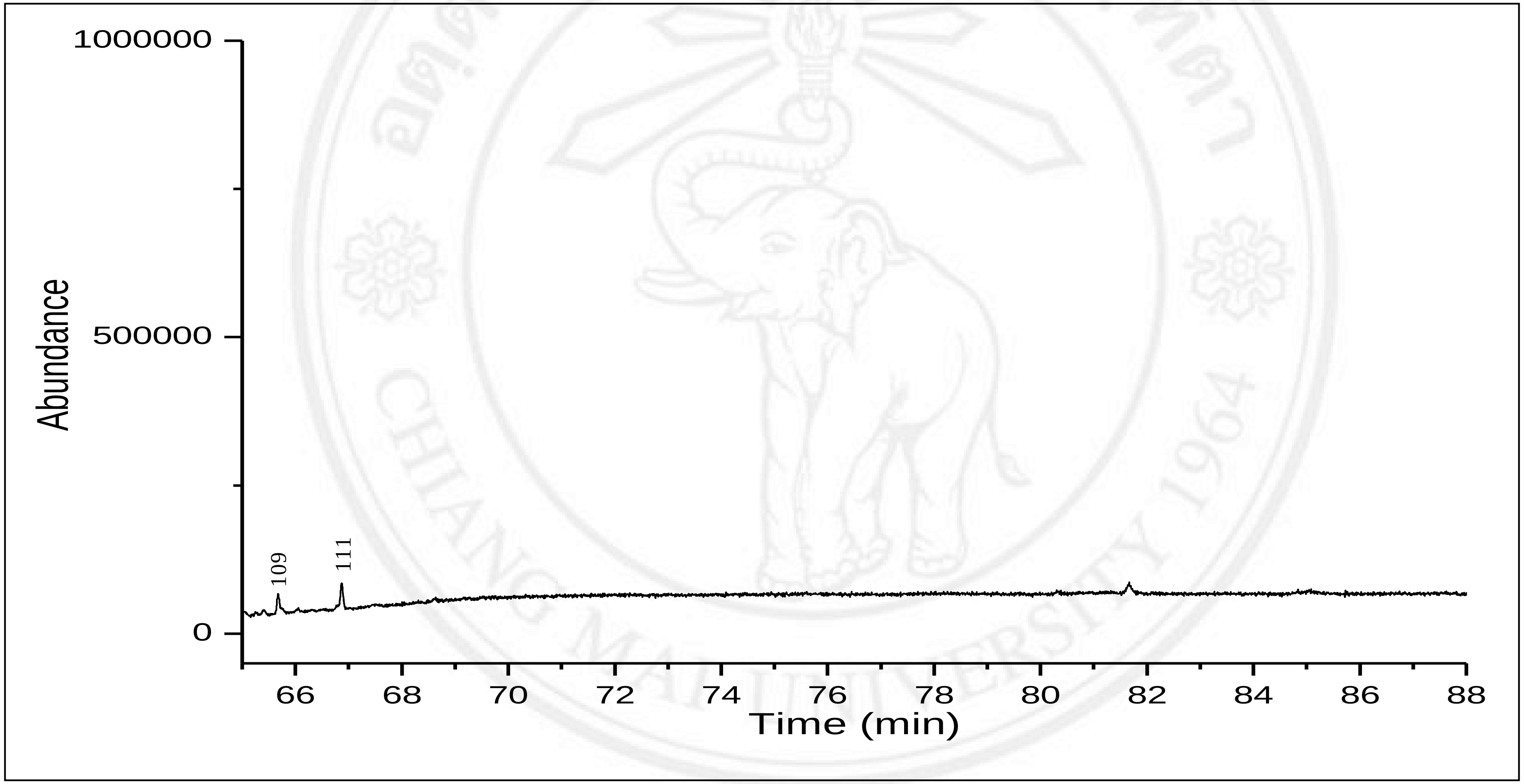

Figure 3.31 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 10 °C/min (continued)

Organic components of bottom layer bio-oil obtained at temperature of 600 °C and heating rate of 10 °C/min are presented in Figure 3.31. Phenolic compounds were the major products which comprised, about 45% of total organic contents. This content was higher than that from the bio-oil obtained at pyrolysis temperatures 400 °C and 500 °C, at heating rate 10 °C/min.

The organic components which were found only in this bio-oil samples, were undecane, 3,4-dimethylphenol, dodecane, 1-docosene and allyl hexadecyl oxalate.

The bio-oil components could not identified by GC-MS but identified by GC×GC-TOF-MS, were ethylbenzene, 3,5-dimethylpyridine, 1-(2-furanyl)ethanone, 2-cyclohexen-1-one, 1-ethynyl-2-methylbenzene, acetophenone, 2-ethylidenecyclo hexanone, naphthalene, isoquinoline, 2-ethyl-6-methylphenol, (1,3-dimethylbutyl) benzene, 1-ethyl-4-methoxybenzene, heptylbenzene, etc.

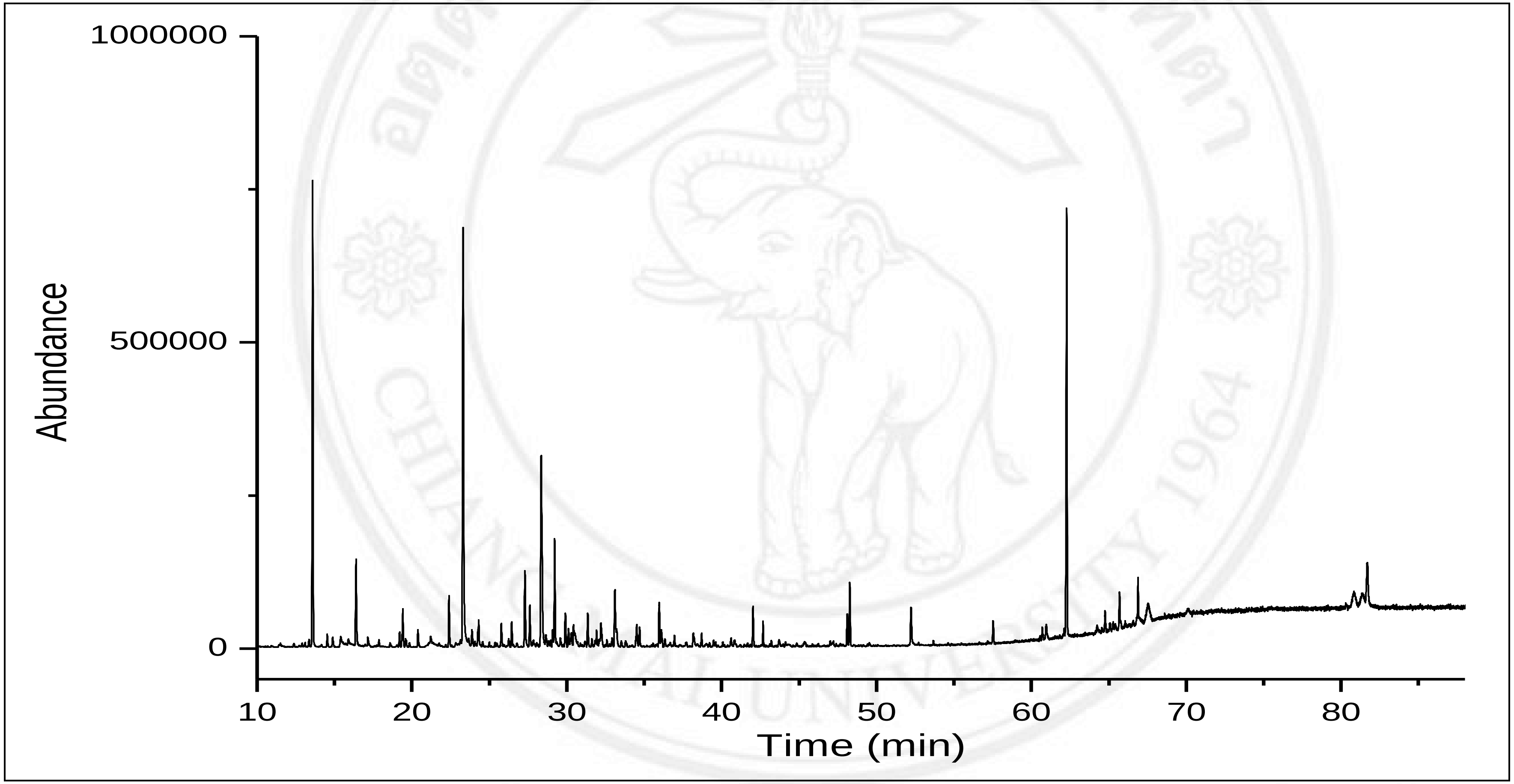

Figure 3.32 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min

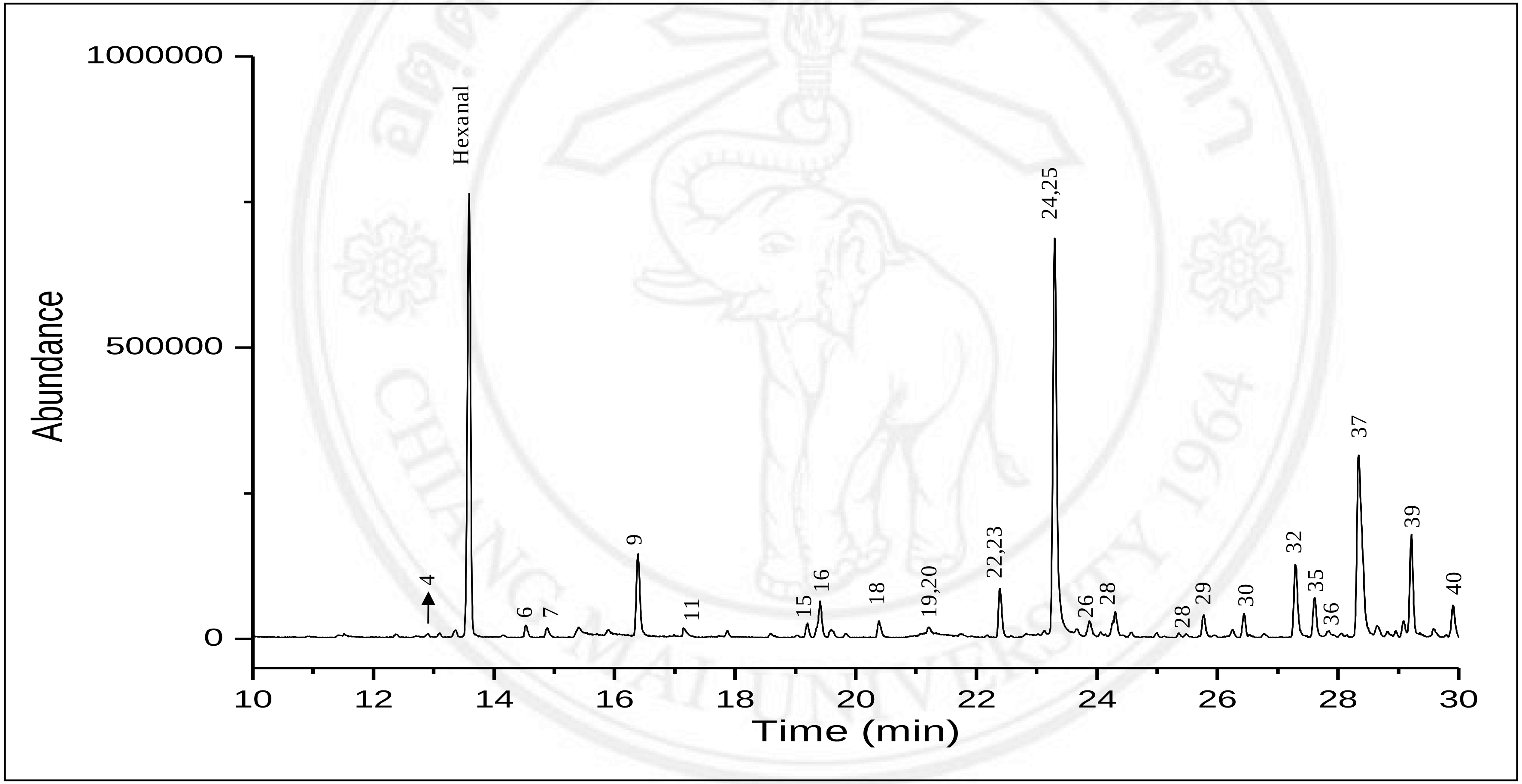

Figure 3.32 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

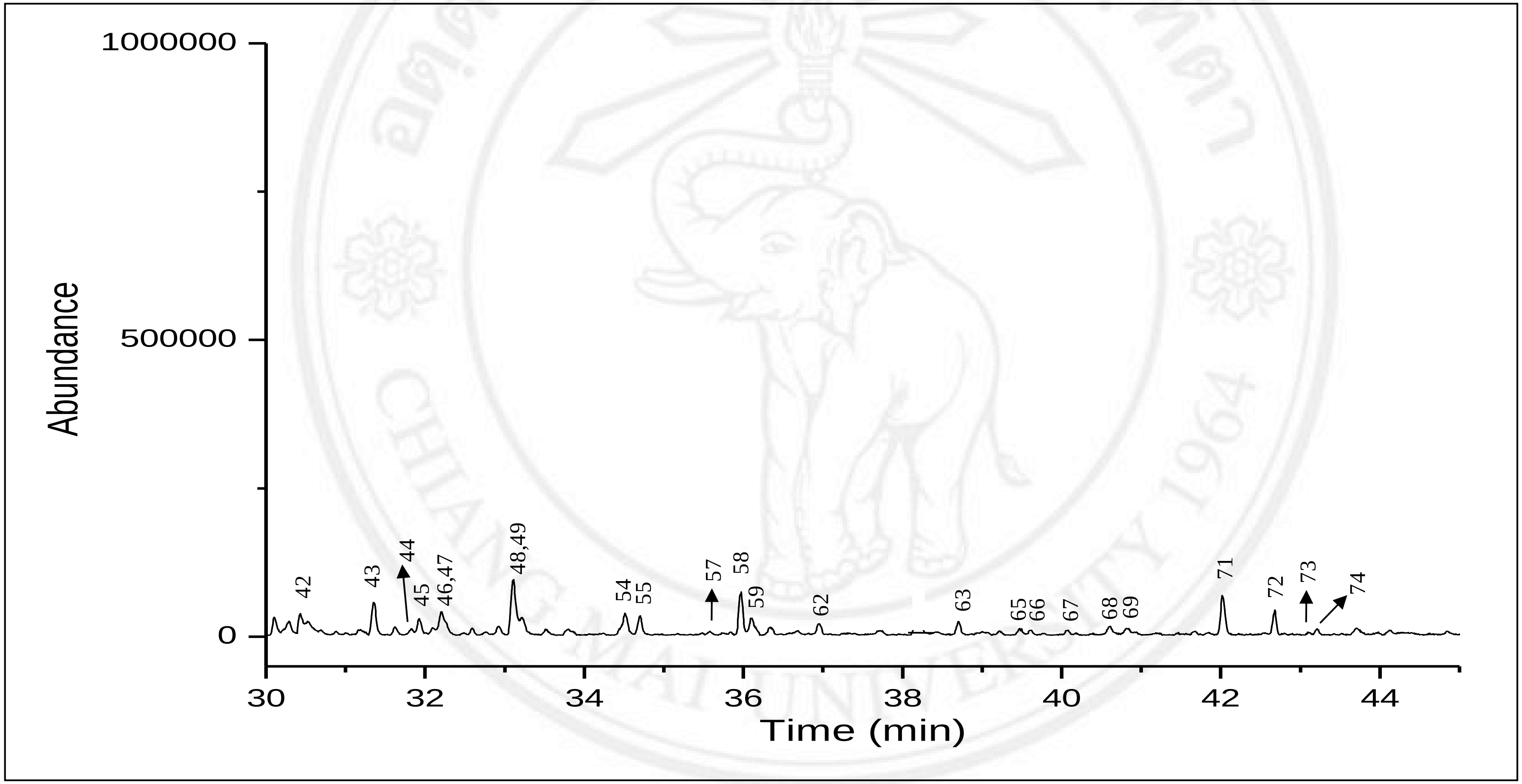

Figure 3.32 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

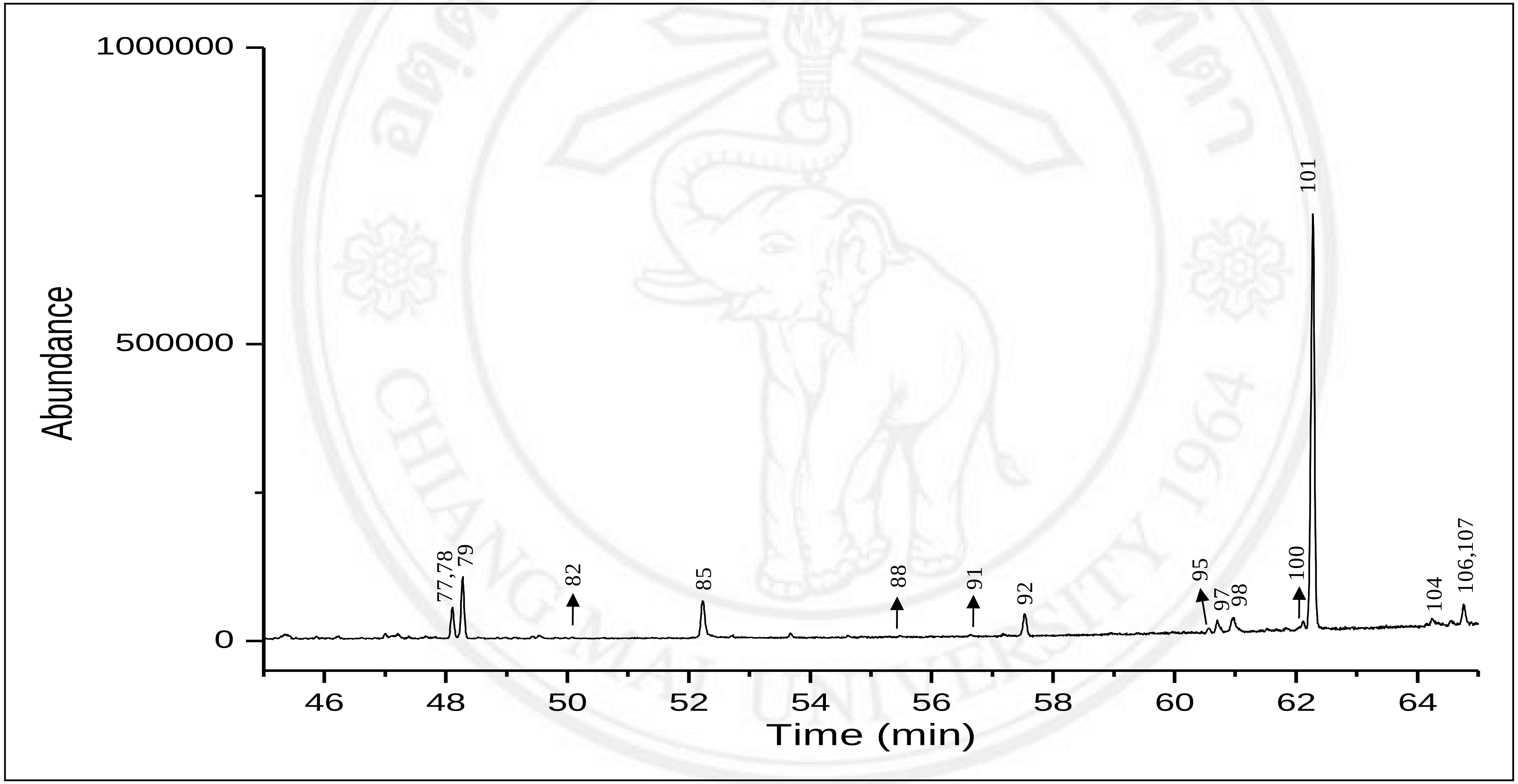

Figure 3.32 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

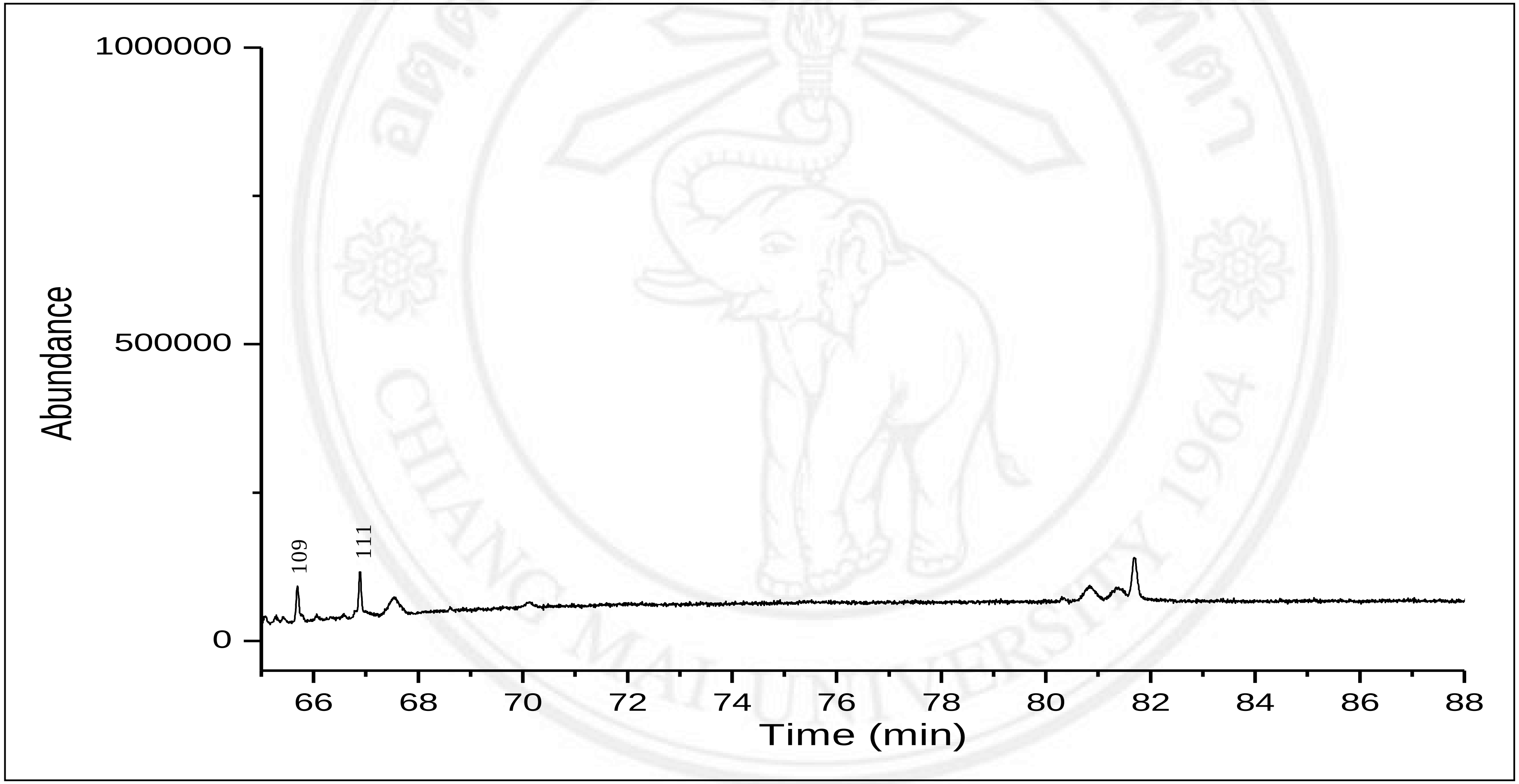

Figure 3.32 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 400 °C and heating rate of 50 °C/min (continued)

Figure 3.32 shows chromatograms of bottom layer bio-oil pyrolysed at temperature of 400 °C and heating rate of 50 °C/min. The result indicated that the major group in the bio-oil was phenolics including, phenol, 2-methylphenol, 4-methylphenol, 2-methoxyphenol, 2,4-dimethylphenol, 4-ethylphenol and 2,6-dimethoxyphenol. The other major compounds were 3,5-dimethylpyridine, caffeine, 1-ethyl-2,5-pyrrolidinedione and 4-methylcyclopentadecanone. An organic compound, 2-methylnaphtalene, was found only in this bio-oil sample.

Many organic compounds could not identified by GC-MS because of the complexity of bio-oil sample, and therefore GC×GC-TOF-MS was chosen for the identification of these compounds, which included 2-hexanone, 4-hydroxy-4-methyl-2-pentanone, ethylbenzene, 1-(2-furanyl)ethanone, 3,5-dimethylpyridine, 2-cyclohexen-1-one, 1-ethynyl-2-methylbenzene, 1-octanol, (2-methyl-2-propenyl)benzene, 3,4-dimethyloctane, benzyl nitrile, 2,5-dimethylphenol, 1-phenyl-1-propanone, 4,7-dimethylbenzofuran, naphthalene, isoquinoline, 2-ethyl-6-methylphenol, (1,3-dimethylbutyl)benzene, heptylbenzene, 1,2,3-trimethylindene, 1-methylnaphthalene, 2-methylnaphthalene, 1-tetradecene, tetradecane, (1-methyldodecyl)benzene, 2-(1-methylethyl)naphthalene, 2,5,9-trimethyldecane, 1-heptadecene, 6-methyl-2-(4-methylpentyl)-1-heptene, 6,10-dimethyl-2-undecanone, 9-octadecenal, 3,7,11,15-tetramethyl-2-hexadecen-1-ol, hexadecanenitrile and 4-methylcyclopentadecanone. Most of them were alcohols, ketones and *N*-,*O*-heterocyclic derivatives.

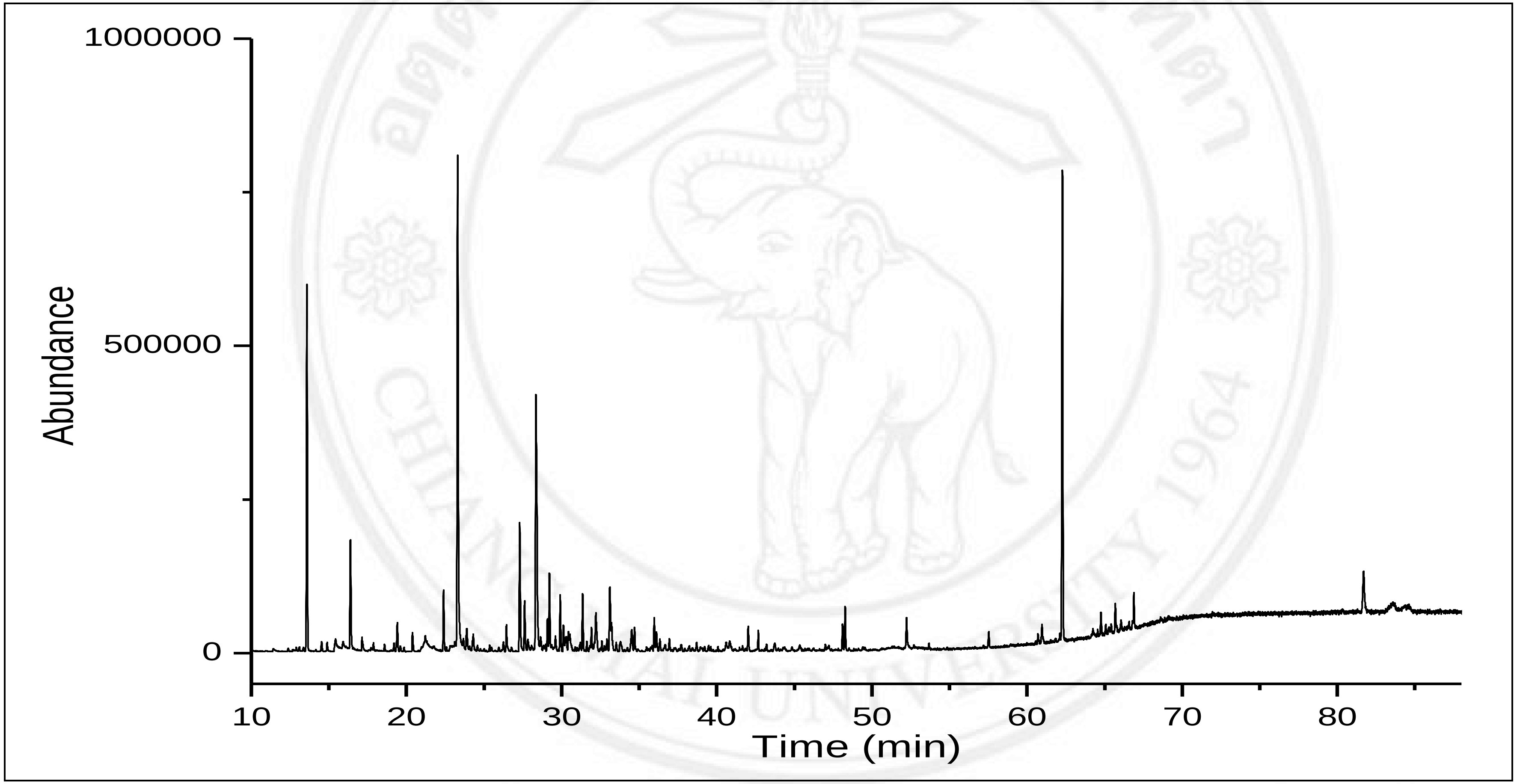

Figure 3.33 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min

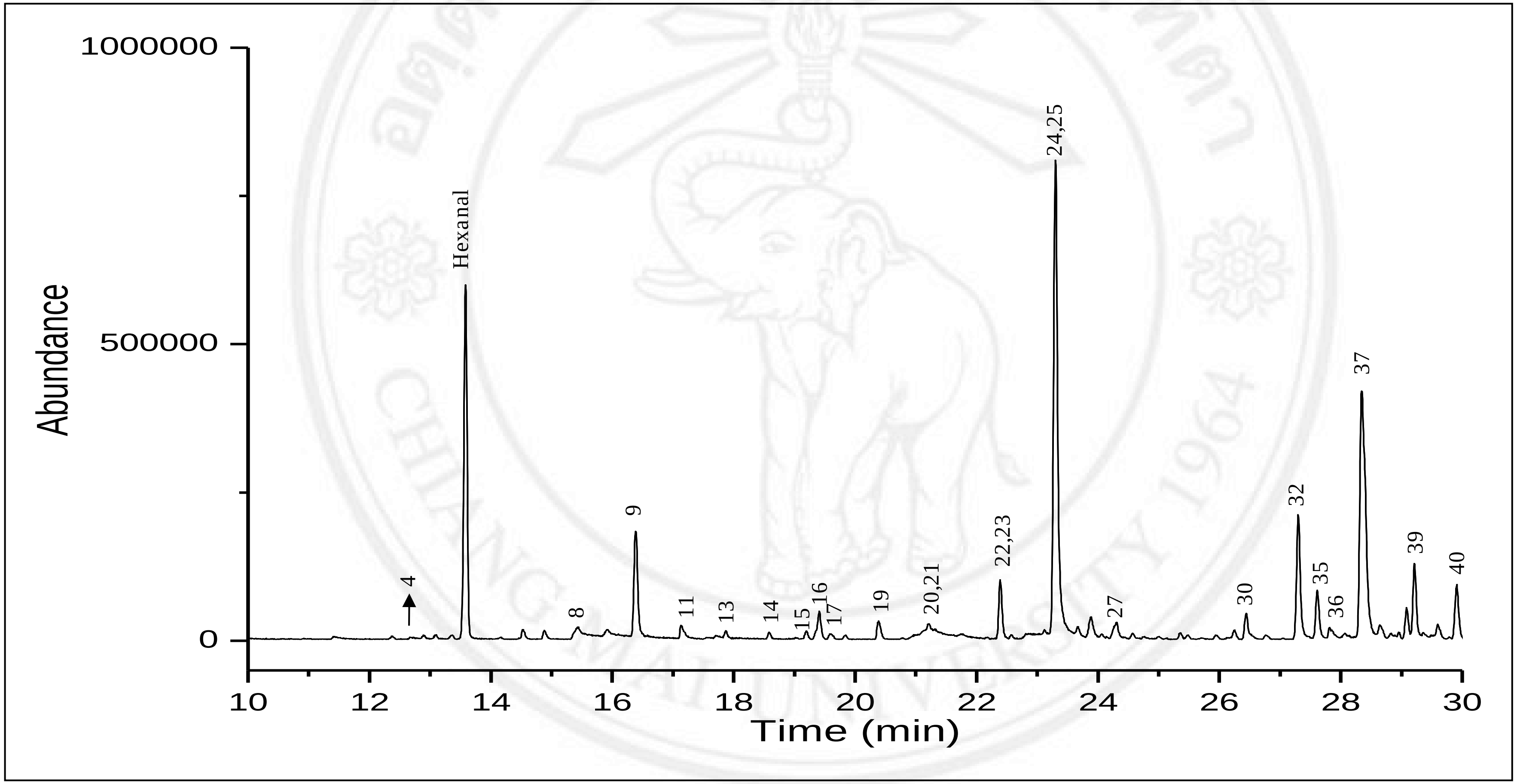

Figure 3.33 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

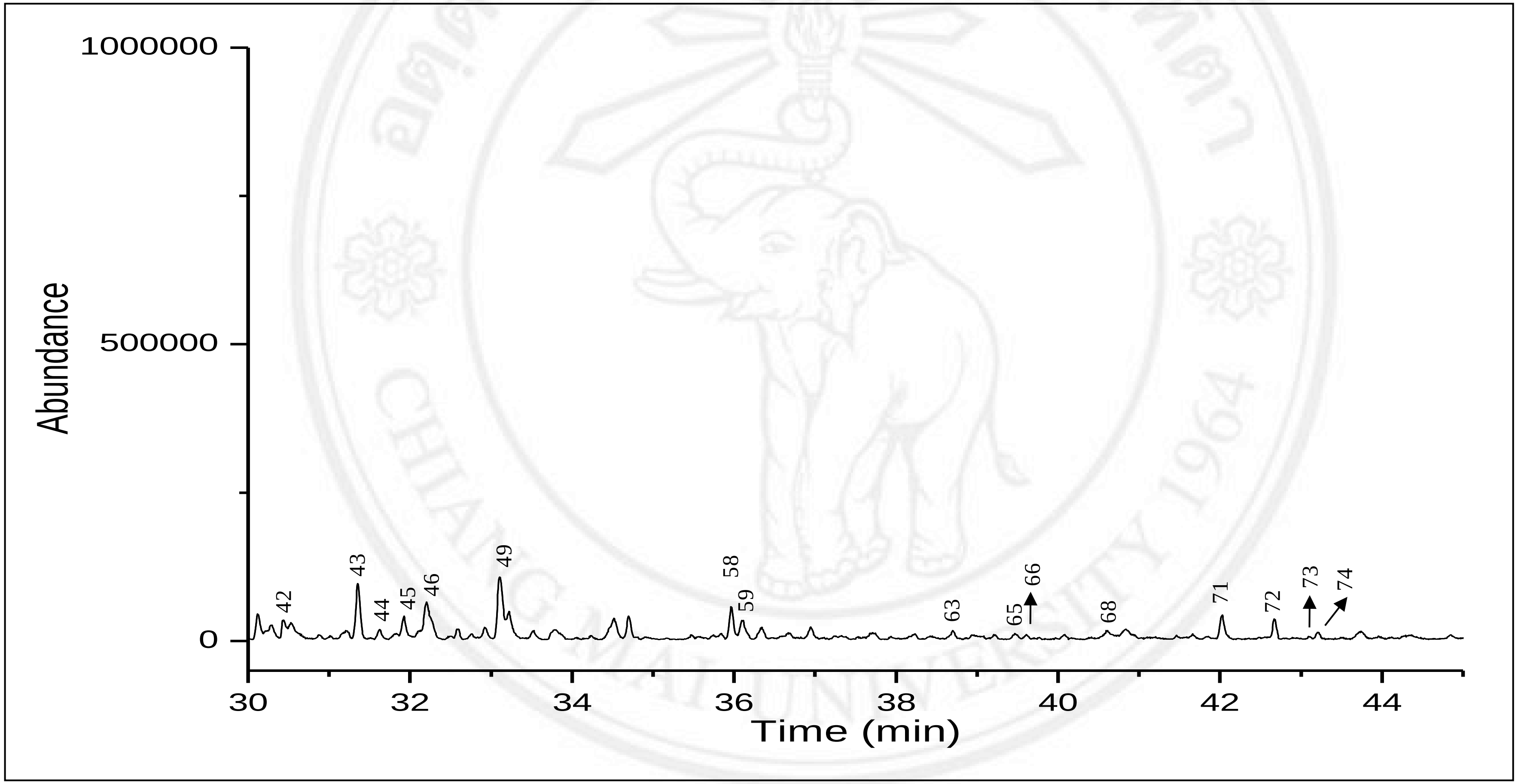

Figure 3.33 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

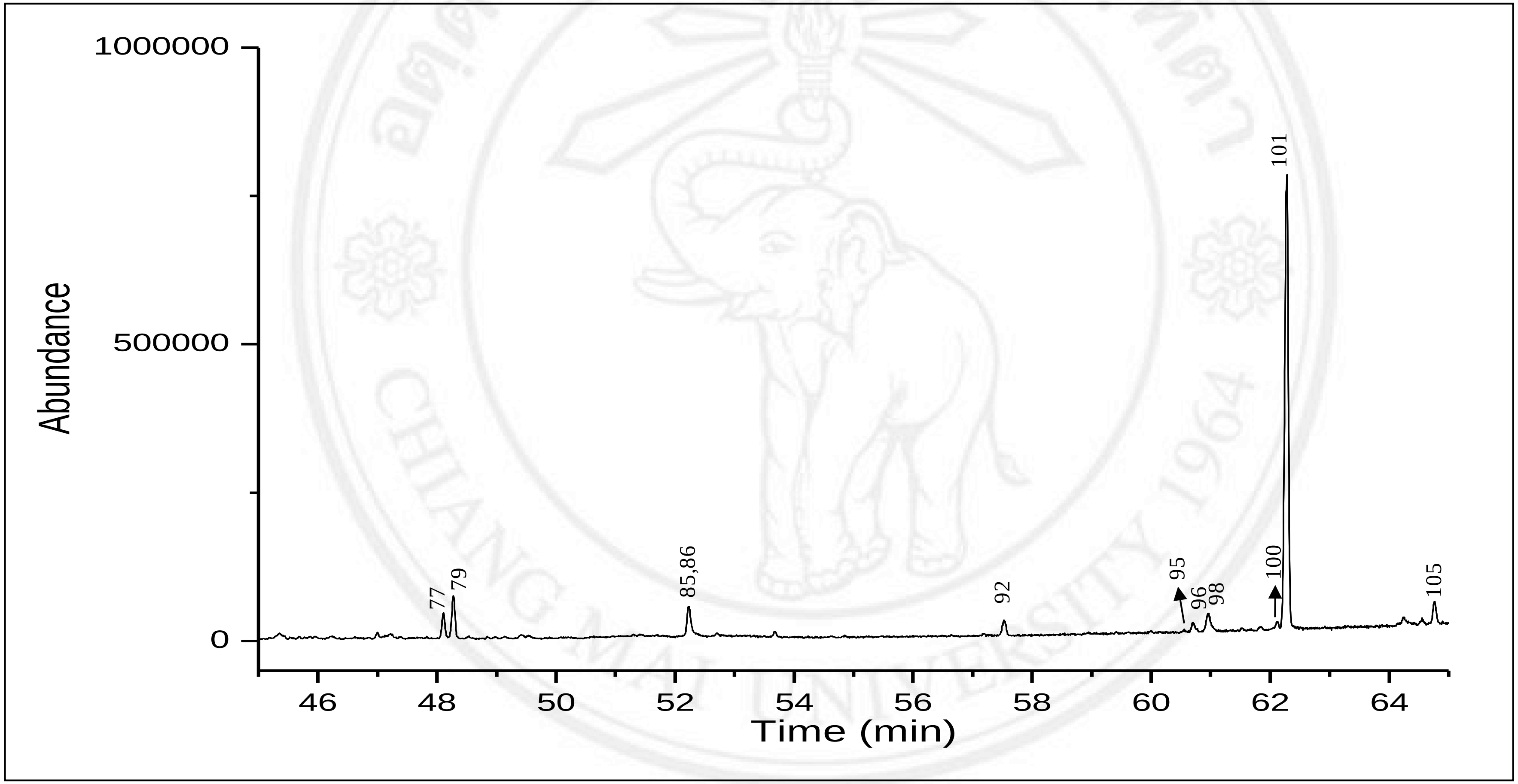

Figure 3.33 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

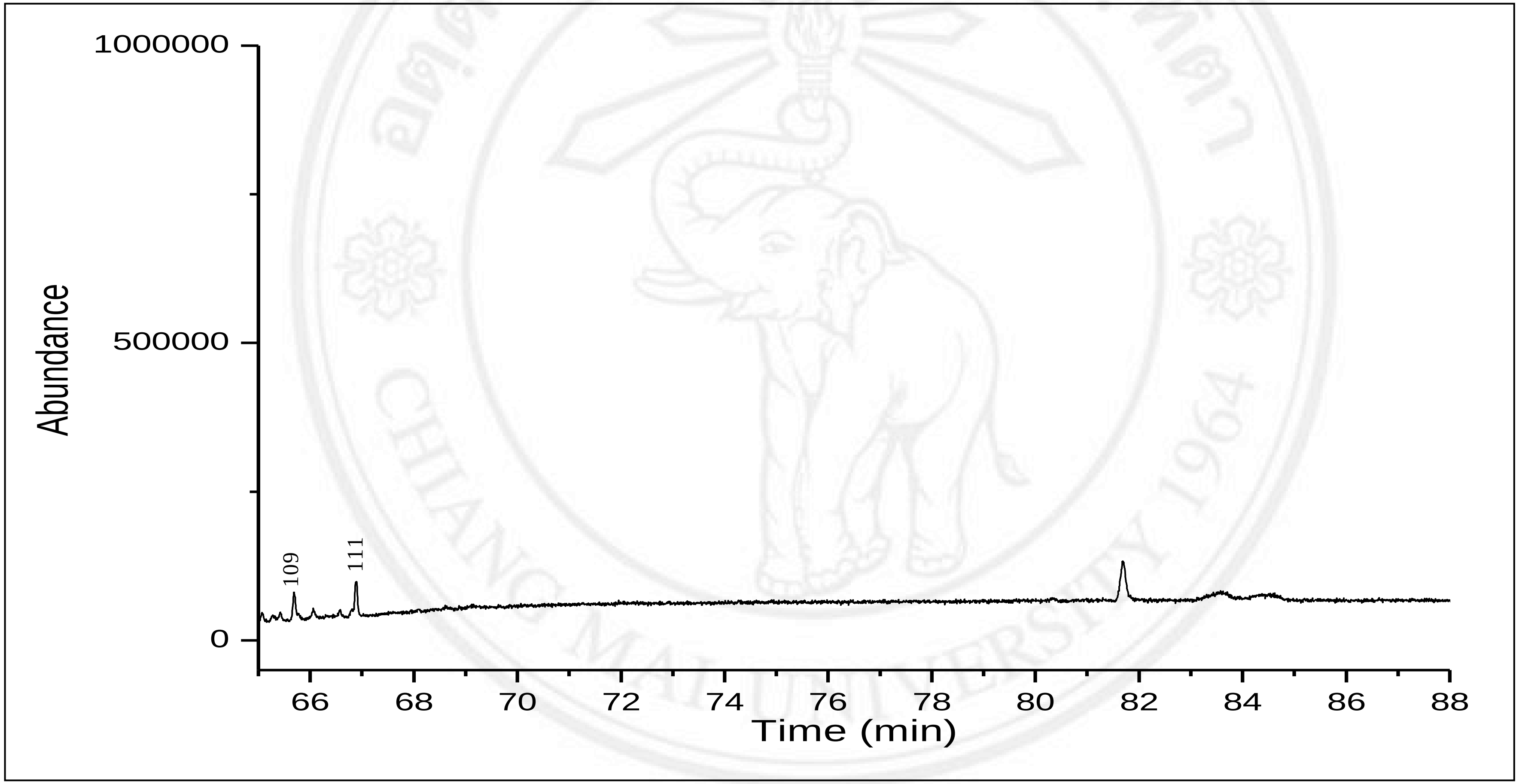

Figure 3.33 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 500 °C and heating rate of 50 °C/min (continued)

From figure 3.33, the major groups of the bio-oil were phenolics, *N*-,*O*-heterocyclic derivatives and ketones, such as 2-hexen-2-one, 2,3-dimethylpyridine, 3,5-dimethylpyridine, phenol 2-methylphenol, 4-methylphenol, 4-ethylphenol, 6,10-dimethyl-2-undecanone, caffeine and 4-methylcyclopentadecanone. Cyclohexanol and 2,4-dimethylpyridine were found only in this bio-oil sample.

The bio-oil components identified by GC×GC-TOF-MS not identified by GC-MS, except those previously reported in the bio-oil from 400 °C, were 2-methyl-2-pentanol, 3-methyl-3-pentanol, 5-hexen-2-one, 2-hexanol, 2-methylcyclopentanone, cyclohexanol, 2,4-dimethylpyridine, propylbenzene, 1-octanol, 1,11-dodecadiene, allylnonyl oxalate, heptadecane, undecanenitrile, 2-tetradecanone and 2,7,10-trimethyldodecane.

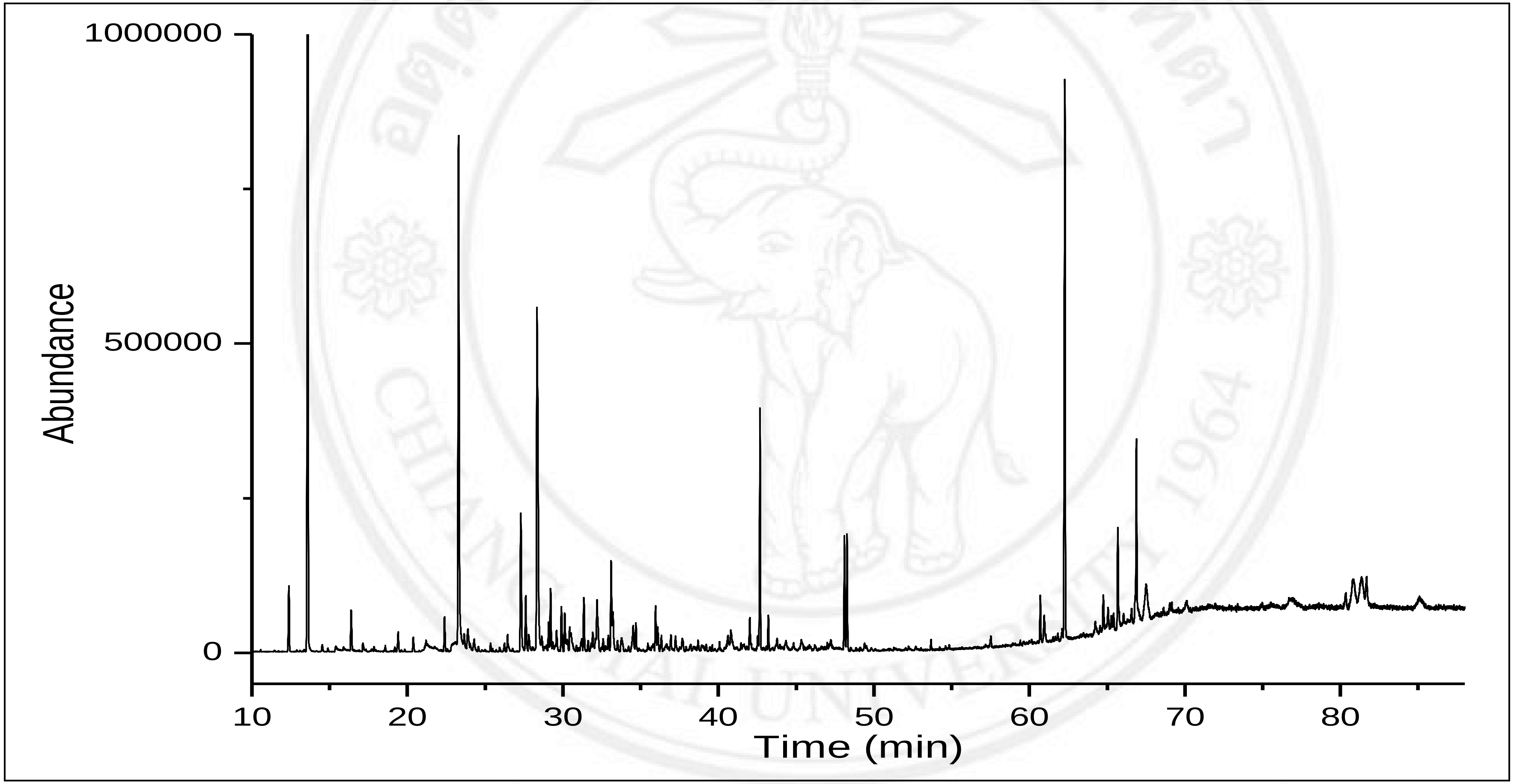

Figure 3.34 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min

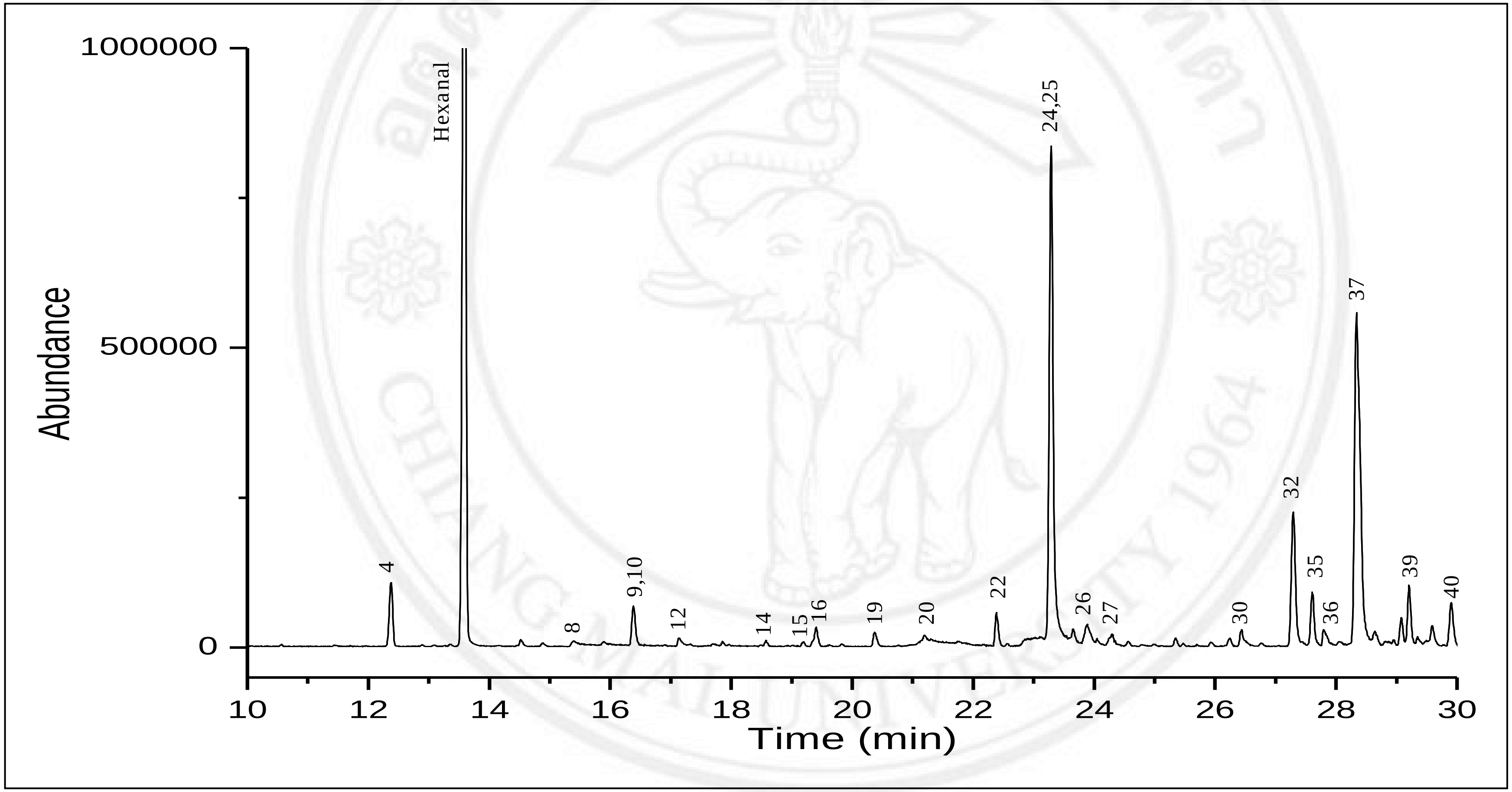

Figure 3.34 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min (continued)

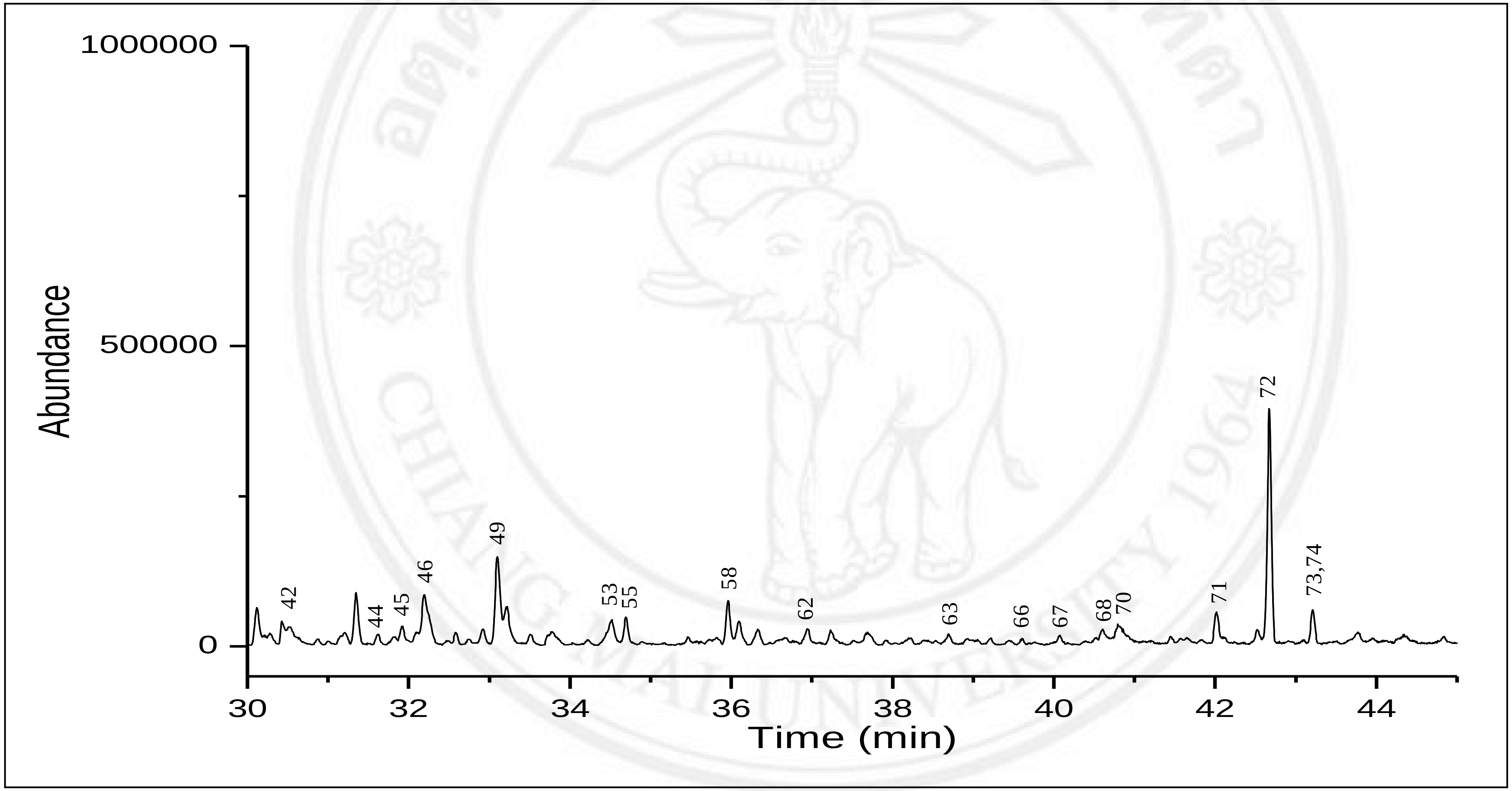

Figure 3.34 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate 50 °C/min (continued)

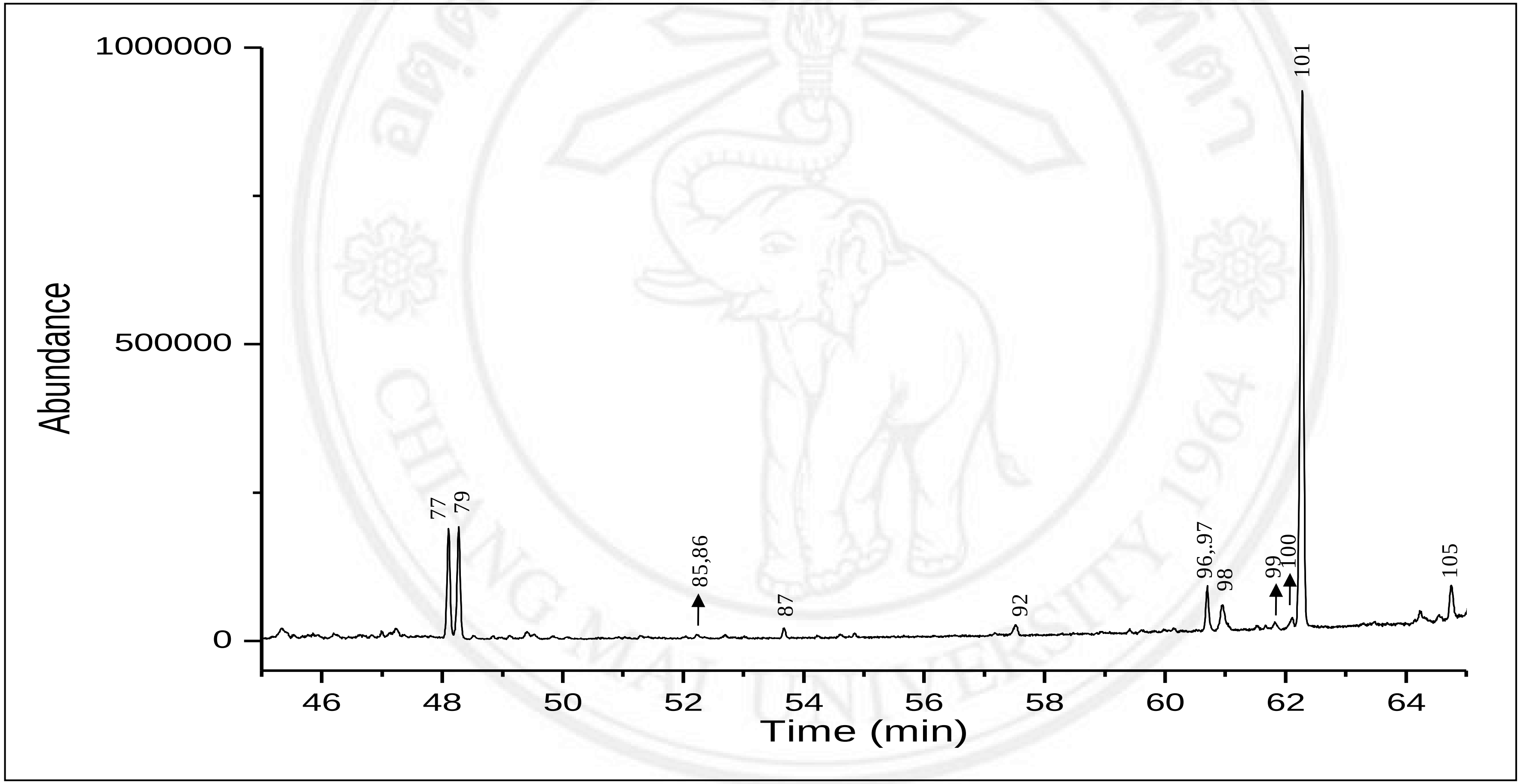

Figure 3.34 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min (continued)

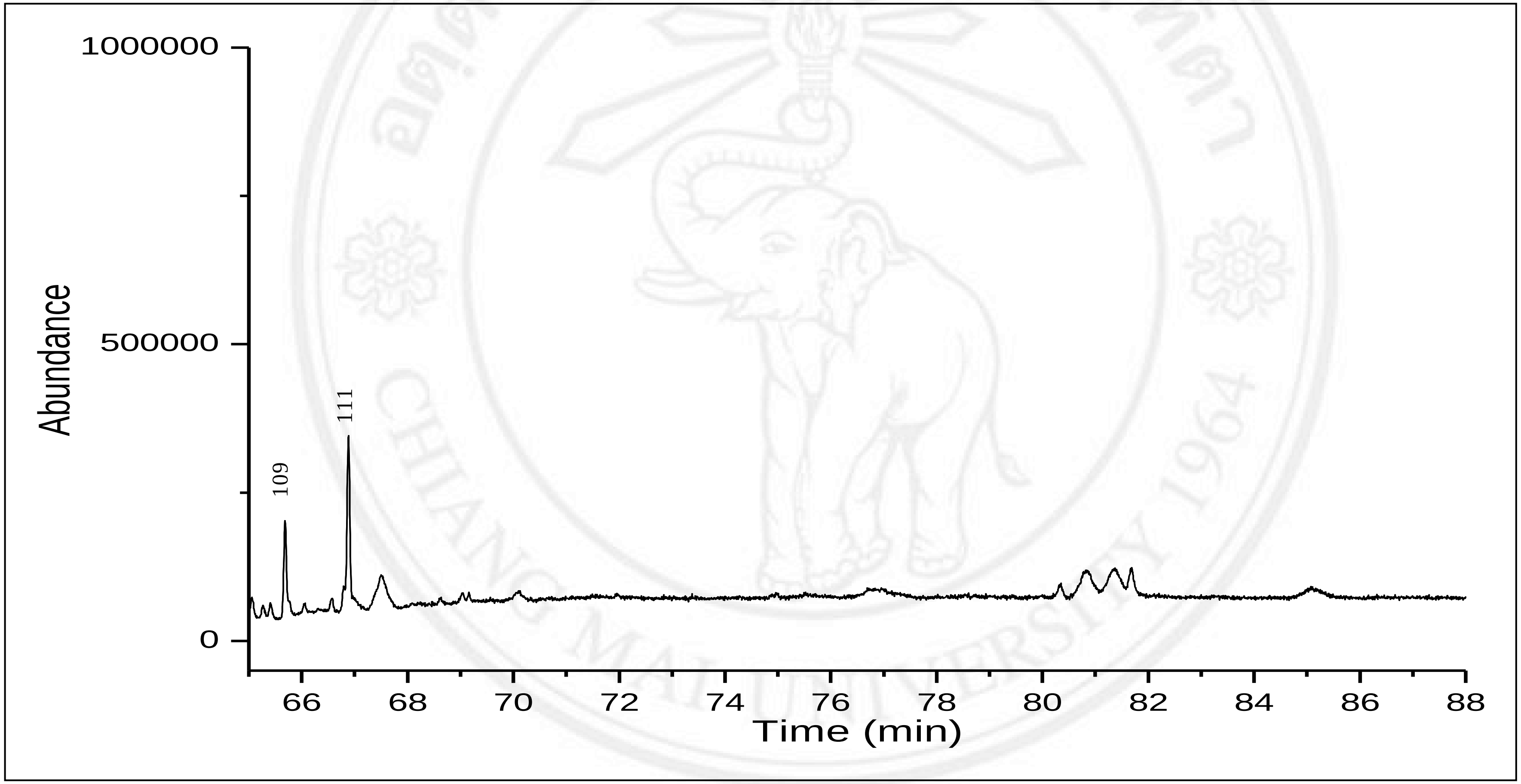

Figure 3.34 GC-MS chromatogram of bottom layer bio-oil obtained using pyrolysis temperatures of 600 °C and heating rate of 50 °C/min (continued)

The organic components of bottom layer bio-oil obtained using pyrolysis temperature of 600 °C and heating rate of 50 °C/min are shown in Figure 3.34. The organic composition of this bio-oil sample is similar to that shown in Figure 3.33. The major components were 2-methyl-2-pentanol, 2-hexanone, phenol, 2-methylphenol, 4-methylphenol, 2-ethylphenol, 2,6-dimethoxyphenol, 4-methylcyclo pentadecanone and caffeine.

The components could not identified by GC-MS, but identified by GC×GC-TOF-MS, were 1-ethyl-4-methoxybenzene, 1,1,3-trimethyl-1H-indene, and methyl oleate, added from listed in 400 °C and 500 °C.

Table 3.2 Structural assignments of components in the bottom layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS

No.	Structural assignment		Molecular formula	LRI	% Relative content					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
1	2-Methyl-2-Pentanol	a	$C_6H_{14}O$	702					1.970	2.184
2	3-Methyl-3-Pentanol	a	$C_6H_{14}O$	729					1.329	1.747
3	5-Hexen-2-one	a	$C_6H_{10}O$	751					2.897	1.687
4	2-Hexanone	a	$C_6H_{12}O$	762	0.235	0.255		0.195	0.469	3.802
5	2-Hexanol	a	$C_6H_{10}O_2$	773					0.160	0.504
6	Unknown	a			4.504			1.550		
7	4-Hydroxy-4-methyl-2-pentanone	a	$C_6H_{12}O_2$	830	1.092			0.491		
8	2-Methylcyclopentanone	a	$C_6H_{10}O$	832					0.707	0.569
9	2-Furanmethanol	b	$C_5H_6O_2$	843	4.113	3.314	0.456	1.362	1.144	0.834
10	Ethylbenzene	a	C_8H_{10}	857		0.215	0.192	0.226	1.155	1.431
11	1,2-Dimethylpyridine	b	$C_7H_{11}N$	860	0.988	0.411	0.315	0.327	0.221	
12	Unknown	a								0.515
13	Cyclohexanol	a	$C_6H_{12}O$	883					0.753	
14	2,3-Dimethylpyridine	b	C_7H_9N	902					5.180	1.958
15	1-(2-Furanyl)ethanone	a	$C_6H_6O_2$	910	1.183		0.342	0.328	0.243	0.072
16	3,5-Dimethylpyridine	a	C_7H_9N	924	0.873	0.325	0.251	4.336	3.174	0.124
17	2,4-Dimethylpyridine	a	C_7H_9N	931					0.257	
18	2-Cyclohexen-1-one	a	C_6H_8O	935	0.855	0.769	0.364	0.500		
19	2,5-Dimethylpyridine	b	C_7H_9N	941				0.675	0.478	0.215
20	Unknown	a			1.584	0.671	0..164	2.496	1.895	1.746

Table 3.2 Structural assignments of components in the bottom layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative content					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
21	Propylbenzene	a	C_9H_{12}	969					0.711	1.613
22	Unknown	a			1.484	1.149	0.214	1.395	3.255	9.190
23	Unknown	a			2.268	2.324	0.401	2.981	1.332	
24	Unknown	a			0.218			0.346	0.214	0.293
25	Phenol	b	C_6H_6O	988	13.189	14.973	19.048	10.257	10.525	13.125
26	2,4,6-Trimethylpyridine	b	$C_8H_{11}N$	998	1.586	0.725	0.466	0.400		0.345
27	Unknown	a			0.629	0.280	0.103	0.486	0.644	0.481
28	Unknown	a			0.523	0.486	0.429	0.432		
29	1-Ethynyl-2-methylbenzene	a	C_9H_8	1046	0.664	0.478	0.195	0.463		
30	2,3-Dimethyl-2-cyclopenten-1-one	b	$C_7H_{10}O$	1048	0.566	0.298	0.553	0.726	0.515	0.558
31	Unknown	a			0.235	0.320	0.378			
32	2-Methylphenol	b	C_7H_8O	1065	0.932	1.654	2.770	2.060	2.301	2.408
33	2-Ethyl-3,5-dimethylpyridine	a	$C_9H_{13}N$	1066	0.241					
34	Acetophenone	a	C_8H_8O	1067		0.132	0.483			
35	1-Octanol	a	$C_8H_{18}O$	1073	2.296	1.860	1.270	1.147	1.002	0.779
36	Unknown	a			0.868	0.485	0.246	0.527	0.345	0.104
37	4-Methylphenol	b	C_7H_8O	1087	6.975	10.053	10.681	7.805	8.861	10.812
38	Undecane	a	$C_{11}H_{24}$	1100			0.319			
39	2-Methoxyphenol	b	$C_7H_8O_2$	1102	6.272	2.561	0.773	3.742	1.033	0.714
40	(2-Methyl-2-propenyl)benzene	a	$C_{10}H_{12}$	1111	0.951	1.035	0.735	1.304	0.621	0.390

Table 3.2 Structural assignments of components in the bottom layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative content					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
41	2-Ethylidenecyclohexanone	a	$C_8H_{12}O$	1115	1.130	1.387	0.781			
42	3,4-Dimethyloctane	a	$C_{10}H_{22}$	1125	0.740	0.740	0.735	0.715	0.337	0.246
43	1-Ethyl-2,5-pyrrolidinedione	b	$C_6H_9NO_2$	1145	2.410	2.879	2.183	2.575	0.657	
44	2-Ethylphenol	b	$C_8H_{10}O$	1147	0.883	1.187	1.773	0.500	0.754	1.388
45	Benzyl nitrile	a	C_8H_7N	1151	0.423	0.522	0.707	0.640	0.313	0.130
46	2,4-Dimethylphenol	b	$C_8H_{10}O$	1158	0.993	1.801	2.377	1.379	1.539	1.548
47	2,5-Dimethylphenol	a	$C_8H_{10}O$	1168		0.198	0.257	0.446		
48	1-Phenyl-1-propanone	a	$C_9H_{10}O$	1177	0.674	0.945	1.361	0.493		
49	4-Ethylphenol	b	$C_8H_{10}O$	1174	2.126	2.517	3.402	2.519	2.947	4.998
50	3,4-Dimethylphenol	b	$C_8H_{10}O$	1181			0.478			
51	Dodecane	a	$C_{12}H_{26}$	1200			0.443			
52	Unknown	a				0.250	0.131			
53	2-Methoxy-4-methylphenol	b	$C_8H_{10}O_2$	1202	0.683	0.539	0.302			0.367
54	4,7-Dimethylbenzofuran	a	$C_{10}H_{10}O$	1207	0.593	0.799	0.898	1.046		
55	Naphthalene	a	$C_{10}H_8$	1208	0.439	1.174	0.974	0.843		0.420
56	Isoquinoline	a	C_9H_7N	1233		0.408	0.272	0.210		
57	2-Ethyl-6-methylphenol	a	$C_9H_{12}O$	1235	0.207	0.242	0.332	0.242	0.386	
58	3,5-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine	b	$C_9H_{12}N_2$	1236	2.826	1.186	0.815	1.168		0.722
59	(1,3-Dimethylbutyl)benzene	a	$C_{12}H_{18}$	1248	0.367	0.359	0.255	0.503	0.344	
60	3-Ethyl-6-methylphenol	a	$C_9H_{12}O$	1260	0.605	0.653				

Table 3.2 Structural assignments of components in the bottom layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative content					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
61	1-Ethyl-4-methoxybenzene	a	$C_9H_{12}O$	1262	0.620	0.408	0.785			0.054
62	Benzenepropanenitrile	b	C_9H_9N	1263		0.551		0.763		0.311
63	4-Ethyl-2-methoxyphenol	b	$C_9H_{19}O_2$	1295	1.331	1.101	0.404	0.830	0.354	0.259
64	Unknown	a			0.590		0.217			0.231
5	Heptylbenzene	a	$C_{13}H_{20}$	1307		0.694	0.842	0.189	0.191	
66	1,2,3-Trimethylindene	a	$C_{12}H_{14}$	1331	0.582	0.642	0.721	0.220	0.272	0.317
67	1-Methylnaphthalene	a	$C_{11}H_{10}$	1321	0.612	0.622	0.692	0.500		0.168
68	Unknown	a				1.853	0.971	0.470	0.340	0.172
69	2-Methylnaphthalene	a	$C_{11}H_{10}$	1379				0.744		
70	1,1,3-Trimethyl-1H-indene	a	$C_{12}H_{14}$	1380	0.410	0.399				0.305
71	2,6-Dimethoxyphenol	b	$C_8H_{10}O_3$	1381	4.221	3.129	2.018	4.349	3.350	2.110
72	2-Butyl-2-octenal	b	$C_{12}H_{22}O$	1386	1.261	2.850	3.041	0.936	0.309	
73	1-Tetradecene	a	$C_{14}H_{28}$	1388	0.711	0.681	0.491	0.834	0.814	0.438
74	Tetradecane	a	$C_{14}H_{30}$	1400		0.629	0.406	0.524	0.334	0.290
75	Unknown	a				0.419				
76	Unknown	a				0.514				
77	(1-Methyldodecyl)benzene	a	$C_{19}H_{32}$	1503	0.623	0.277	0.392	0.631	0.361	1.287
78	2-(1-Methylethyl)naphthalene	a	$C_{13}H_{14}$	1505	0.512	0.376		0.256		
79	Unknown	a			1.013	1.429	1.460	2.272	1.848	1.358
80	(Z)-3-Tetradecene	a	$C_{14}H_{28}$	1518		0.653				

Table 3.2 Structural assignments of components in the bottom layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative content					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
81	Dibenzofuran	a	$C_{12}H_8O$	1521	0.416	0.270				
82	Unknown	a				0.433	0.249	0.167	0.300	0.348
83	Unknown	a				0.530				
84	Nonylbenzene	a	$C_{15}H_{24}$	1554		0.353				
85	2,5,9-Trimethyldecane	a	$C_{13}H_{28}$	1592		0.240		0.267	0.266	0.244
86	1,11-Dodecadiene	a	$C_{12}H_{22}$	1597		0.218			0.315	0.166
87	Allyl nonyl oxalate	a	$C_{14}H_{24}O_4$	1653					0.218	0.175
88	1-Heptadecene	a	$C_{17}H_{34}$	1683		0.523	0.273	0.236	0.213	0.162
89	Unknown	a				0.191				0.161
90	Heptadecane	a	$C_{17}H_{36}$	1700		0.510	0.305		0.262	
91	6-Methyl-2-(4-methylpentyl)-1-heptene	a	$C_{14}H_{28}$	1734		0.641	0.437	0.239	0.159	
92	6,10-Dimethyl-2-undecanone	a	$C_{13}H_{26}O$	1780	1.880	0.569		2.087	2.081	1.254
93	Undecanenitrile	a	$C_{11}H_{21}N$	1793		0.402			0.298	
94	2-Tetradecanone	a	$C_{14}H_{28}O$	1805		0.411			0.327	
95	9-Octadecenal	a	$C_{18}H_{34}O$	1821	0.645	1.407	4.091	0.824	1.771	1.639
96	2,7,10-trimethyldodecane	a	$C_{15}H_{32}$	1826	0.590	0.448			0.214	0.200
97	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	a	$C_{20}H_{40}O$	1835	1.134	0.556	0.497	0.465		0.211
98	3,7,11,15-Tetramethyl-2-hexadecene	b	$C_{20}H_{40}$	1836		3.035	1.470	1.185	0.566	0.423
99	Methyl oleate	a	$C_{19}H_{36}O_2$	1842		0.419	0.502			0.199
100	Unknown	a			0.573	0.630	0.713	0.070	0.064	0.276

Table 3.2 Structural assignments of components in the bottom layer of tea waste bio-oils analyzed by GC-MS and GC×GC-TOF-MS (continued)

No.	Structural assignment		Molecular formula	LRI	% Relative content					
					Heating rate (10 °C/min)			Heating rate (50 °C/min)		
					400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
101	Caffeine	b	$C_8H_{10}N_4O_2$	1867	6.638	5.575	5.655	8.063	8.033	7.357
102	Hexadecanenitrile	a	$C_{16}H_{31}N$	1911	1.345	1.355	1.464	0.801	0.461	0.265
103	Methyl hexadecanoate	a	$C_{17}H_{34}O_2$	1913	3.124					
104	Unknown	a						0.644		
105	Unknown	a				0.468	0.665		0.055	0.111
106	Unknown	a			1.511			0.761		
107	Unknown	a					1.694	0.840		
108	Unknown	a			0.596					
109	Unknown	a			2.697	1.416	1.420	1.557	2.106	2.363
110	2-Methyloctadecane	a	$C_{19}H_{40}$	2033	1.266	0.553	0.439			
111	4-Methylcyclopentadecanone	a	$C_{16}H_{30}O$	2047	1.766	3.827	4.736	2.815	4.633	4.716
112	1-Docosene	a	$C_{22}H_{44}$	2107			0.733			
113	Allyl hexadecyl oxalate	a	$C_{21}H_{38}O_4$	2176			0.764			

a Found in GC×GC not GC

b Found in GC×GC and GC

The identified components of the bottom layer from various pyrolysis process are listed in Table 3.2. Using of GC×GC-TOF-MS technique, the identified components increased from 57% to 78%. The major groups in the bottom layer were phenolics, ketones and *N*-,*O*-heterocyclic derivatives, as seen in Figure 3.35. The ketones compounds which were found as the major compounds in the bottom layer were 1-ethyl-2,5-pyrrolidinedione, 2-butyl-2-octenal, 9-octadecenalม 6,10-dimethyl-2-undecanone and 4-methylcyclopentadecanone.

Significantly, hydrocarbons were found in the bottom layer of bio-oil with lower % relative contents than those of the top layer because the top layer is usually organic phase while the bottom layer is aqueous phase.

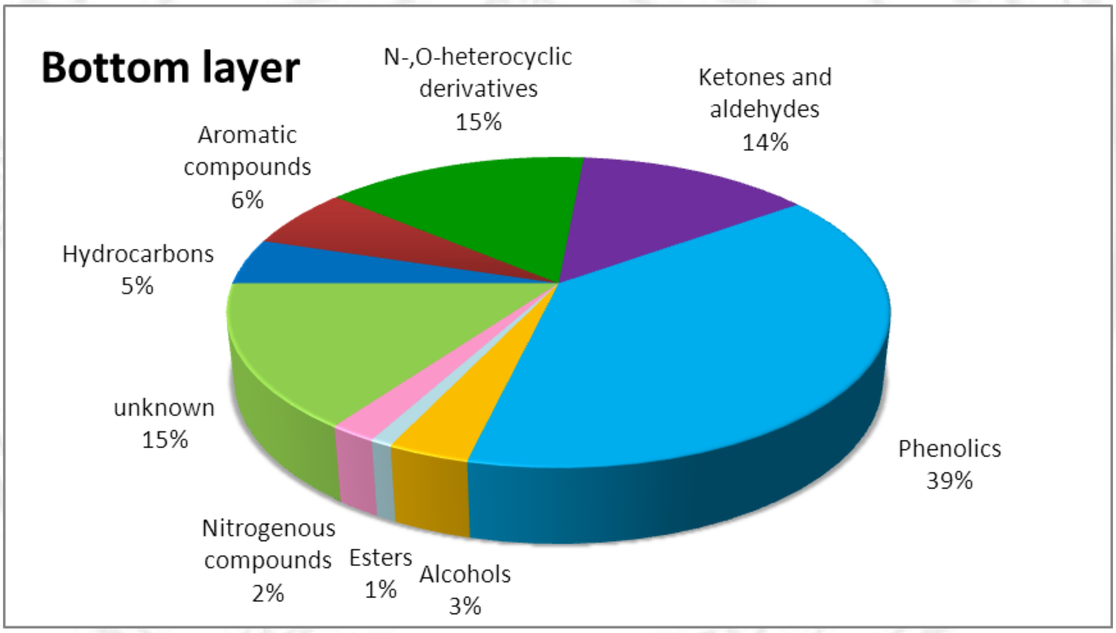

Figure 3.35 Comparison of the percent relative amounts of each chemical group in the bottom layer of bio-oil samples

3.4. Comparative studies on the organic components in the bio-oil samples from tea waste obtained by various pyrolysis processes

For the reason that hydrocarbons are the types of organic compounds that provide enegy for use as fuel, the effects of pyrolysis temperature and heating rate on content of hydrocarbons were observed in particular. The relative contents of compounds in group of phenolics as a major product in both layer of bio-oil were also observed and discussed.

3.4.1 Effect of temperature

The effect of increasing temperature was determined, as shown in Table 3.1 and Table 3.2. The lists of organic compounds of bio-oils obtained using heating rate of 10 °C/min and various pyrolysis temperatures are presented in Figures 3.36-3.38.

It is shown in Figures 3.36-3.37 that the relative contents of hydrocarbons decreased as the pyrolysis temperature was raised up because hydrocarbons were degraded at high temperature whereas the relative contents of most phenolic compounds increased. The hydrocarbons that were significantly decreased by high temperature were pentadecane, 1-pentadecene, 1-heptadecene and 3,7,11,15-tetramethyl-2-hexadecene. The phenolics that significantly increased by high temperature were phenol, 4-methylphenol and4-methylphenol. Furthermore, the relative contents of methoxy phenol isomers such as 4-methyl-2-methoxyphenol and 2-methoxyphenol were decreased when temperature was raised. This result agreed with Demirbas[39] who studied the influence of temperature on the compounds obtained from olive husk, hazelnut shell, spruce wood and beech wood via pyrolysis. The same trend of phenolics can be observed in the bottom layer of the bio-oil as shown in Figure 3.38.

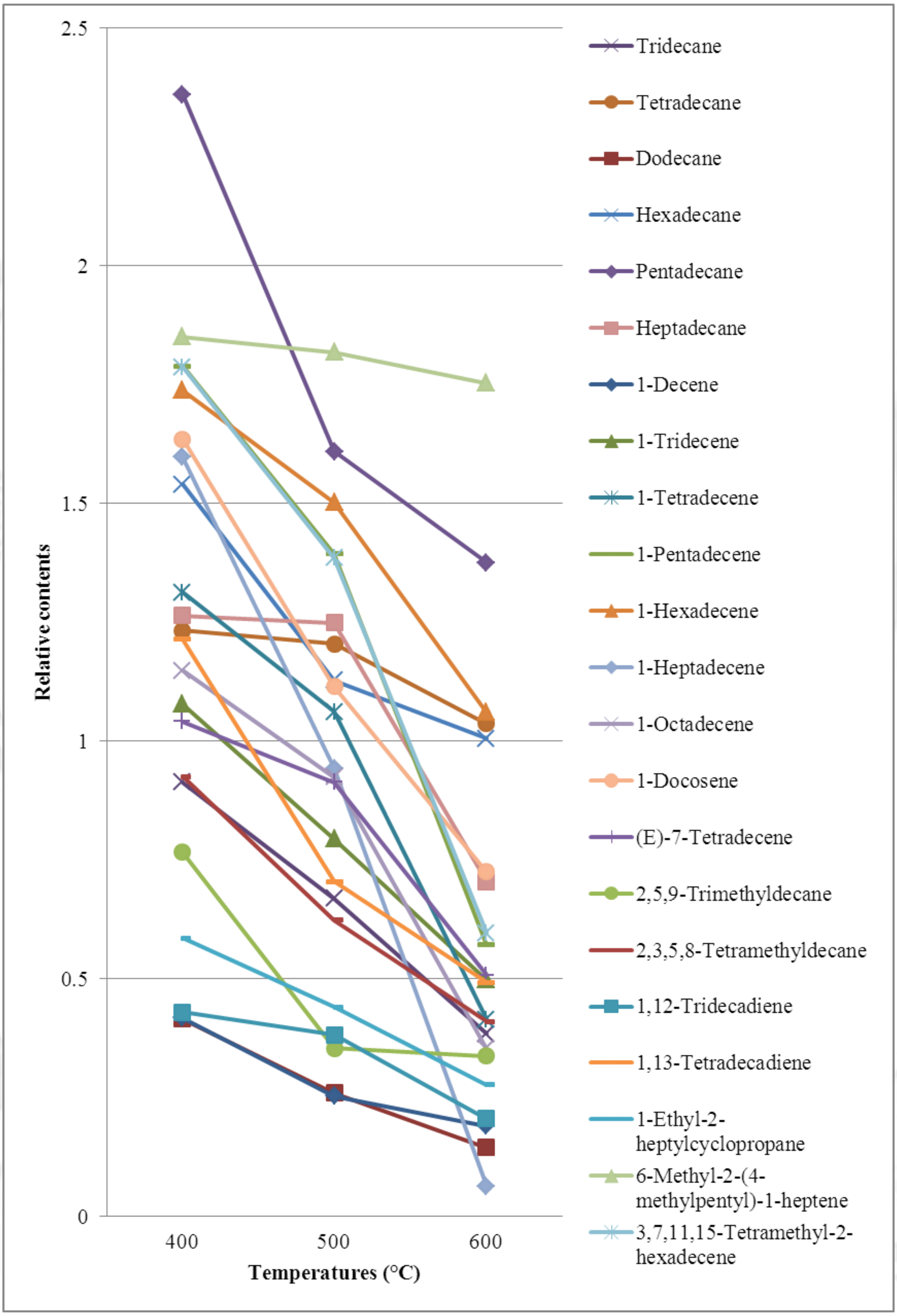

Figure 3.36 Effect of the temperature on the hydrocarbons compounds of bio-oil obtained from the top layer at the heating rate of 10 °C/min

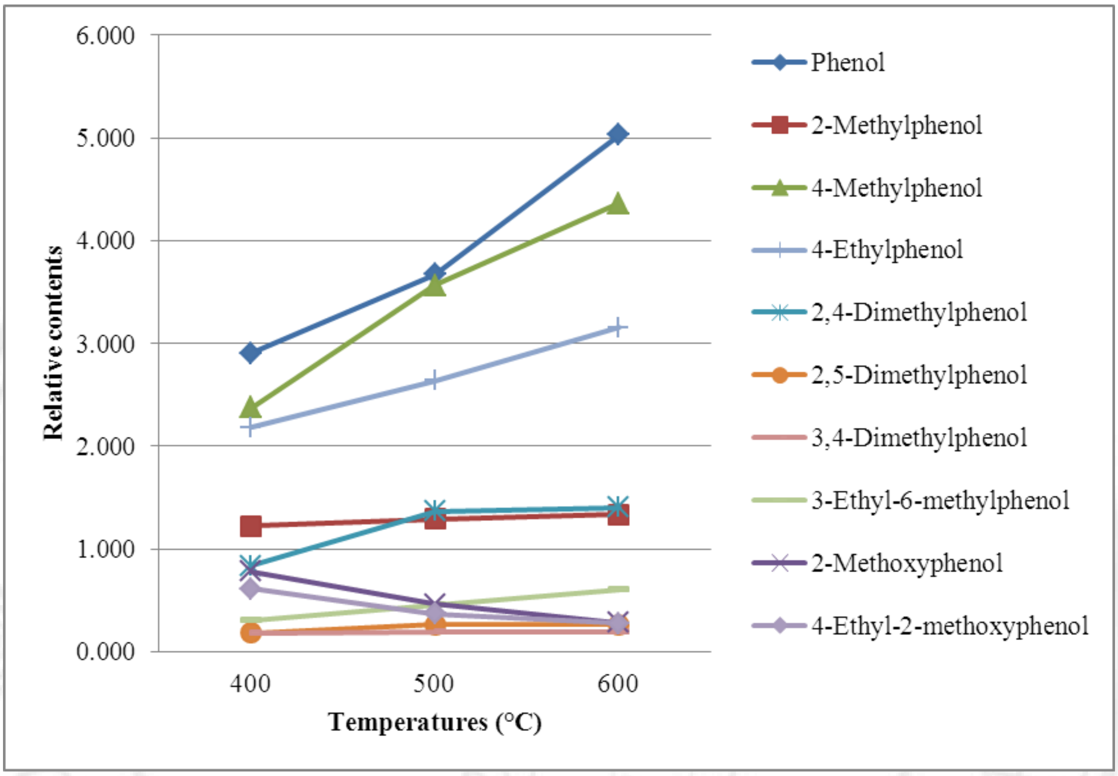

Figure 3.37 Effect of the temperature on the phenolics contents of bio-oil obtained from the top layer at the heating rate of 10 °C/min

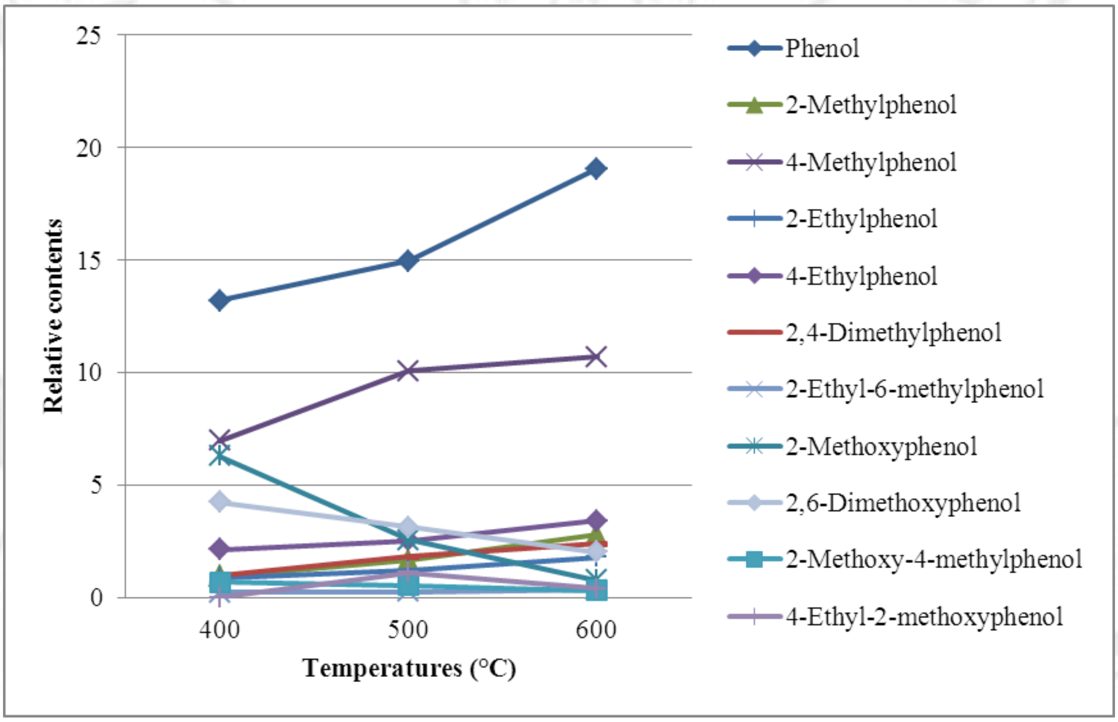

Figure 3.38 Effect of the temperature on the phenolic compounds of bio-oil obtained from the bottom layer at the heating rate of 10 °C/min

The effect of pyrolysis temperature on number of the organic components found in the top layer bio-oil obtained using heating rate of 50 °C/min is presented in Figures 3.39-3.41. By raising the temperatures from 400to 600 °C, the relative contents of hydrocarbons decreased except a few such as 2,3,5,8-tetramethyldecane, (Z)-3-tetradecene and (Z)-5-tetradecene.If the temperature was increased more than 600 °C, the number and contents of most hydrocarbons tended to decrease. Besides these hydrocarbons, the content of other compounds including 2,3-dimethylpyridine, 4-methylcyclopentadecanone and 3,7,11,15-tetramethyl-2-hexadecen-1-ol significantly decreased by the increase of temperature as shown in Table 3.1.

A rise of pyrolysis temperature had affected on the contents of phenolics, aromatic compounds, ketones and *N*-,*O*-heterocyclic derivatives. The changing of their relative contents was not clearly visible because of their very low relative contents. Similar results were obtained at the heating rate of 10 °C/min.

In observation of the pyrolysis temperature at 400 °C, hydrocarbons had high contents. However, the contents of phenolic compounds were not significantly different among the temperatures of 400-600 °C. Therefore, the temperature of 400 °C is the most appropriated one for the pyrolysis of tea-waste.

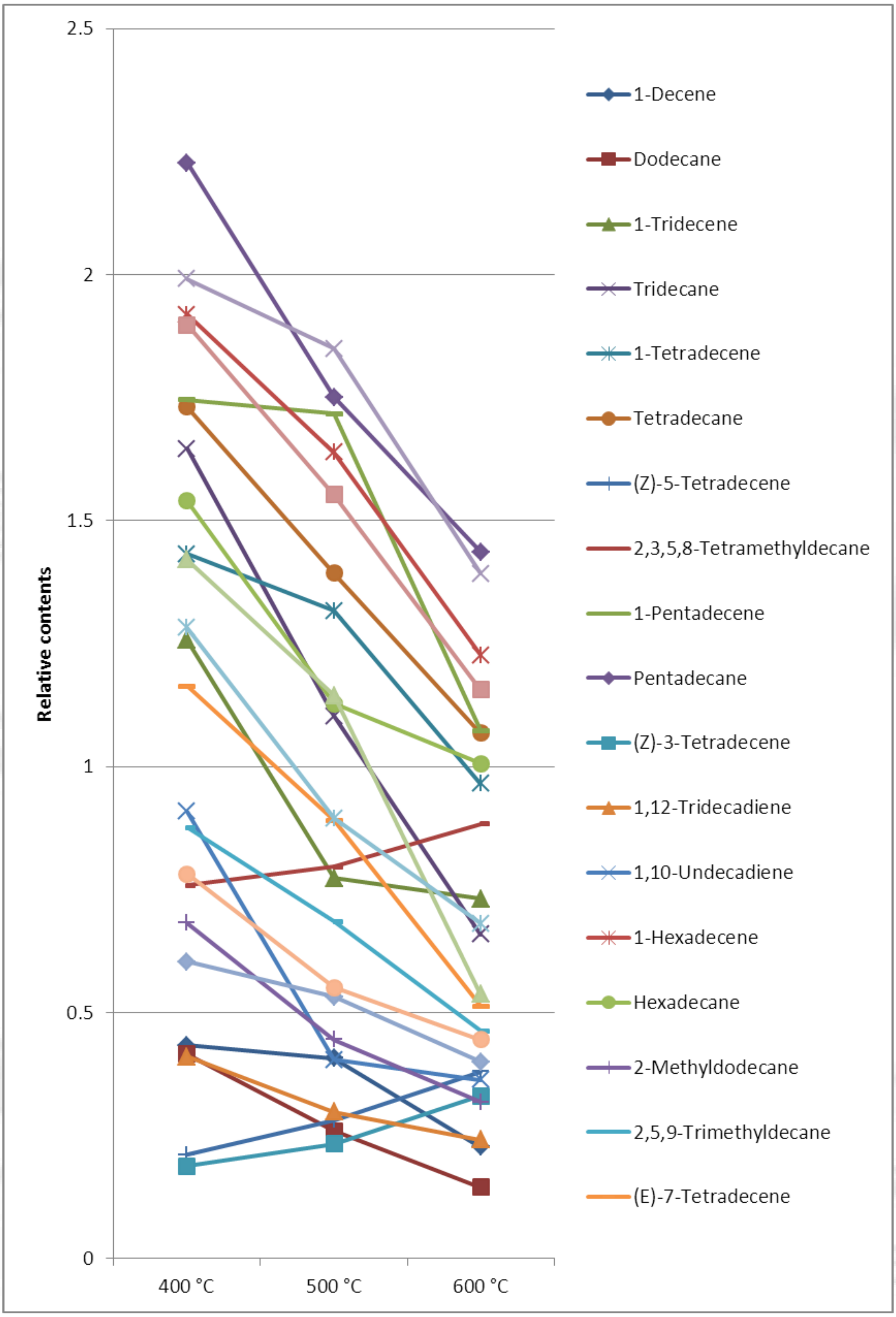

Figure 3.39 Effect of the temperature on the content of the hydrocarbons compounds of bio-oils obtained from the top layer at the heating rate of 50 °C/min

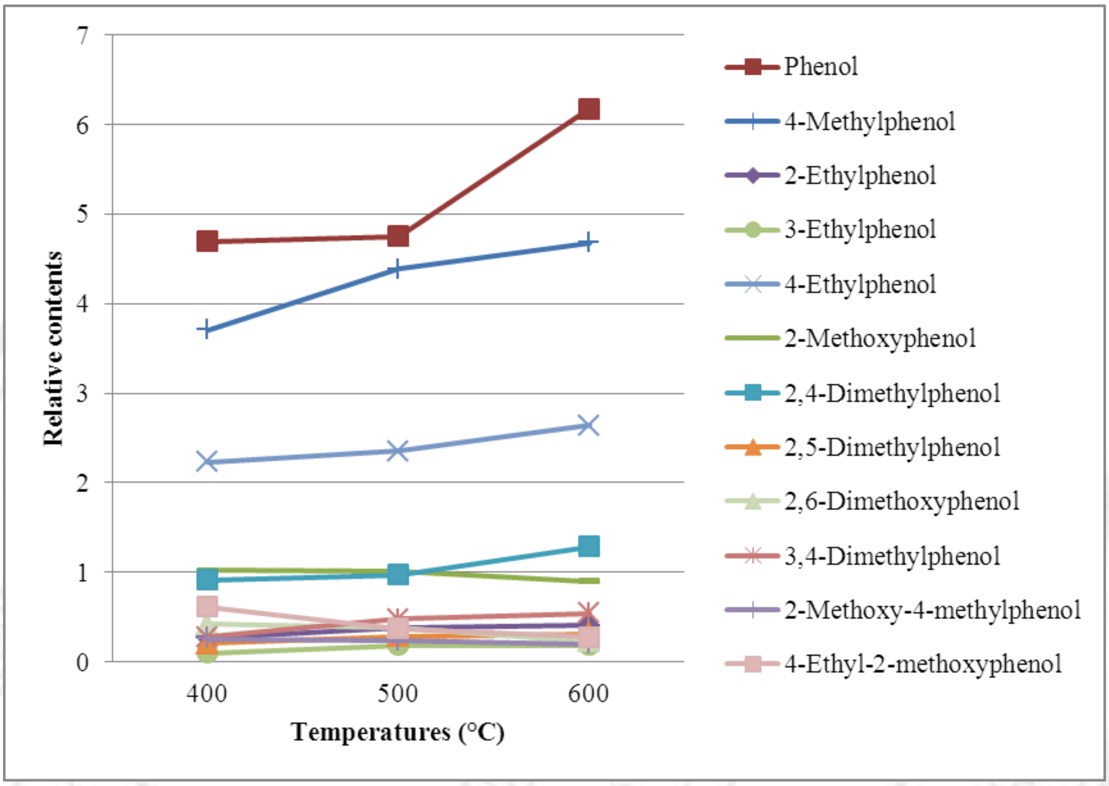

Figure 3.40 Effect of the temperature on the content of the phenolic compounds of bio-oils obtained from the top layer at the heating rate of 50 °C/min

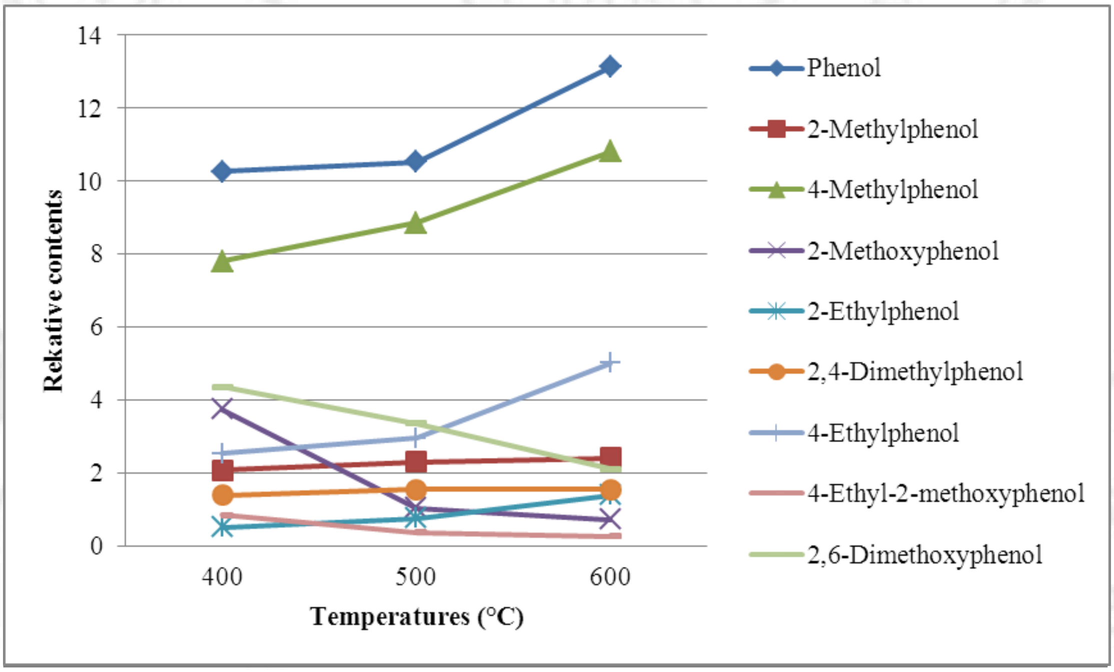

Figure 3.41 Effect of the temperature on the phenolic compounds of bio-oils obtained from the bottom layer at the heating rate of 50 °C/min

3.4.2 Effect of heating rates

The heating rate was found to play an important role on the relative contents of the organic components as can be seen in Figures 3.42-3.44. Hydrocarbons and phenolic contents obtained at the low pyrolysis temperature of 400 °C from the top layer were comparatively observed in terms of heating rate. Increasing the heating rate from 10 to 50 °C/min had increased the relative contents of the organic components mainly in the groups of hydrocarbons, phenolics, aromatic compounds and *N*-, *O*-heterocyclic aromatic derivatives.

Effects of increasing heating rate on the contents of hydrocarbons were shown in Figures 3.42-3.43. The results revealed that the hydrocarbons contents increased with the increase of heating rate from 10 to 50 °C/min except some few hydrocarbons. The hydrocarbons that their contents were clearly increased such as tridecane and tetradecane as can be seen in Figure 3.42. Contents of some hydrocarbons that significantly decreased when increasing the heating rate were 2,3,5,8-tatramethyldecane and 1-docosene as shown in Figure 3.43. Increasing the heating rate from 10 to 50 °C/min, the contents of phenolics increased as presented in Figure 3.44, which were phenol and 4-methylphenol.

It can be concluded that the rapid heating of the biomass favors more polymerization of the cellulose and the formation of volatiles than slow heating. So volatiles that condensed at the heating rate of 50 °C/min appeared in higher amounts than the heating rate of 10 °C/min. Whereas, contents of these organic compounds found at heating rate 50 °C/min were not significantly different from those found at heating rate 10 °C/min. The pyrolysis process using the heating rate of 50 °C/min takes less time than the heating rate of 10 °C/min. Hence, the heating rate of 50 °C/min is more appropriate for the pyrolysis of tea waste.

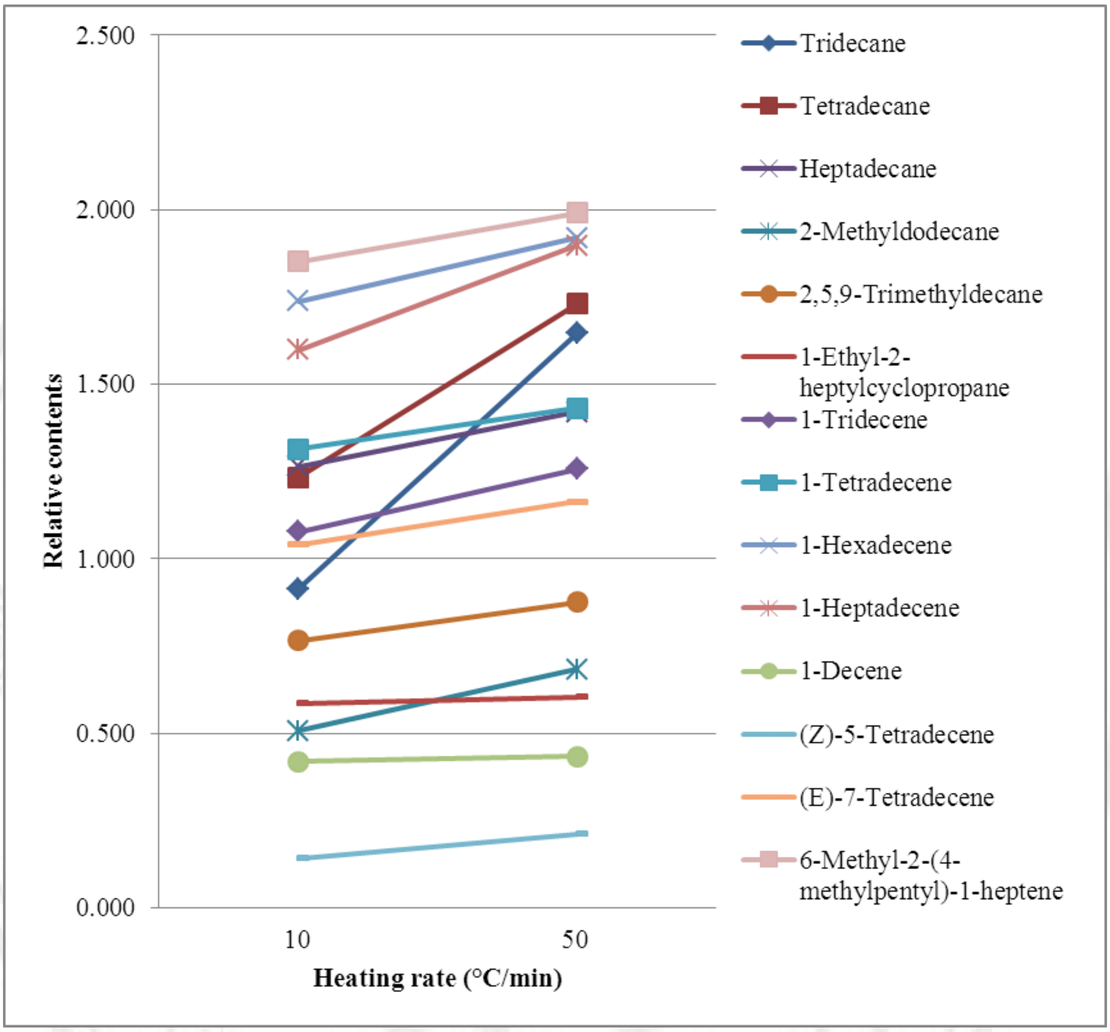

Figure 3.42 Effect of the heating rates on the increasing of hydrocarbons contents

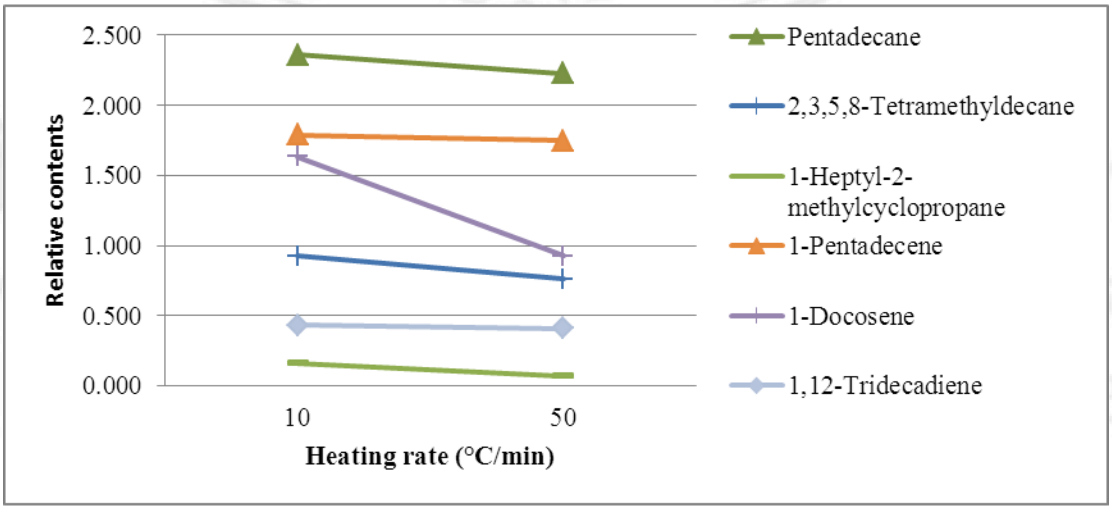

Figure 3.43 Effect of the heating rates on the decreasing of hydrocarbons contents

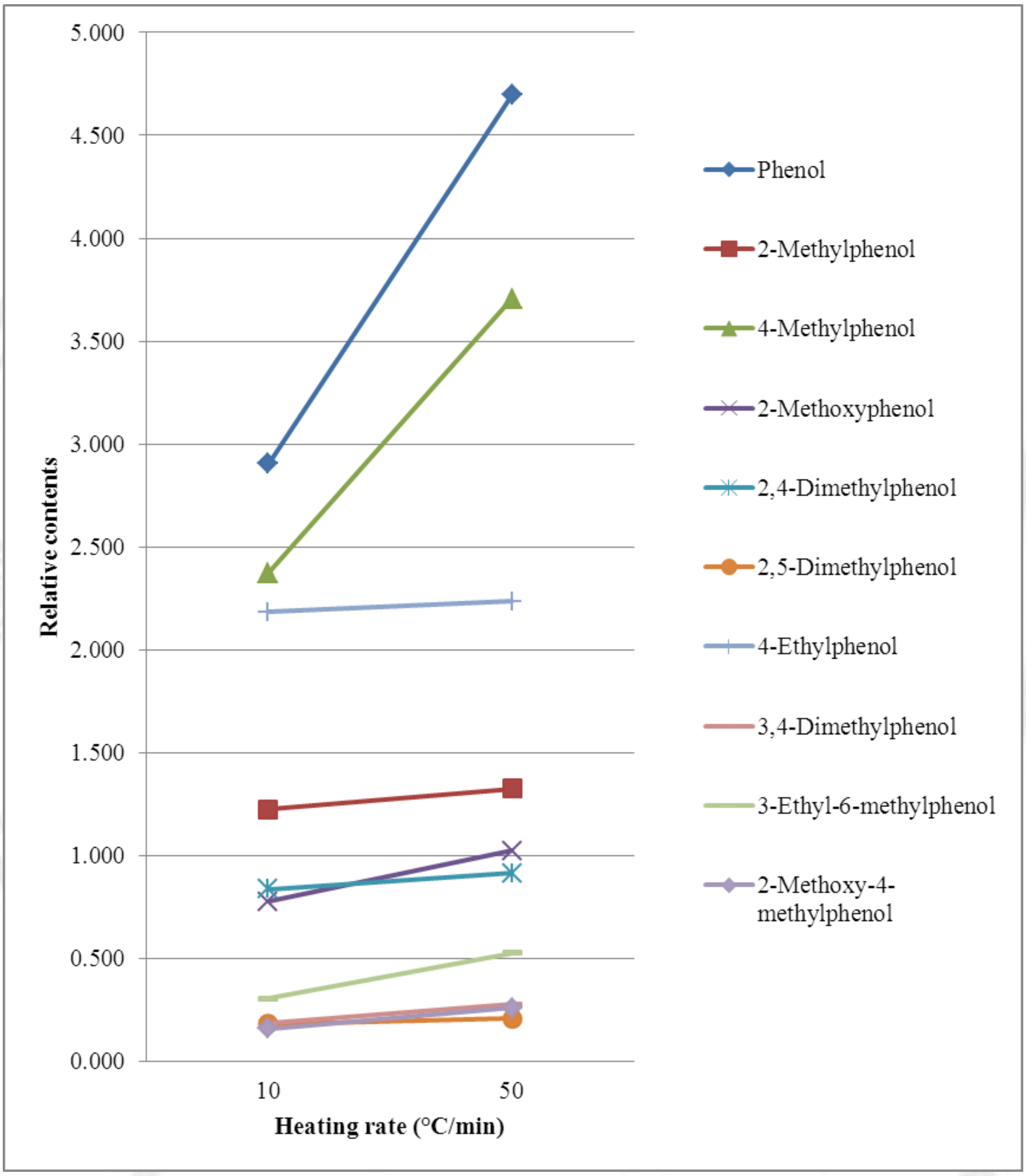

Figure 3.44 Effect of the heating rates on phenolics contents