

Gas chromatographic–mass spectrometric study of the oil fractions produced by microwave-assisted pyrolysis of different sewage sludges

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Abstract

The pyrolysis of sewage sludge was studied in a microwave oven using graphite as microwave absorber. The pyrolysis temperature ranged from 800 to 1000 °C depending on the type of sewage sludge. A conventional electrical furnace was also employed in order to compare the results obtained with both methods. The pyrolysis oils were trapped in a series of condensers and their characteristics such as elemental analysis and calorific value were determined and compared with those of the initial sludge. The oil composition was analyzed by GC–MS. The oils from the microwave oven had *n*-alkanes and 1-alkenes, aromatic compounds, ranging from benzene derivatives to polycyclic aromatic hydrocarbons (PAHs), nitrogenated compounds, long chain aliphatic carboxylic acids, ketones and esters and also monoterpenes and steroids. The oil from the electric oven was composed basically of PAHs such as naphthalene, acenaphthylene, phenanthrene, fluoranthene, benzo[*a*]anthracene, benzofluoranthenes, benzopyrenes, indeneperylene, benzo[*ghi*]perylene, and anthanthrene. In contrast, these compounds were not produced in the case of microwave-assisted pyrolysis.

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1. Introduction

The problem of sewage sludge disposal is proving to be one of the most complex environmental problems of today. The most common disposal methods currently used are landfilling, farmland applications and incineration, none of which are exempt from drawbacks [1].

As an alternative, the pyrolysis of sewage sludge is receiving increasing attention as an economic and

environmentally acceptable route to waste disposal [2–6]. The products of pyrolysis are gas, oil and carbonaceous residue. The gas can be used as fuel [7]. The carbonaceous residue can also be burnt as fuel, disposed of—since the heavy metals are fixed inside the carbonaceous matrix—or be upgraded to activated carbon [8,9]. The oil can either be used as fuel or as raw material for chemicals [10]. Another important characteristic of pyrolysis is that the processing conditions can be optimized to maximize the production of one or another fraction [7,11]. The production of pyrolysis oils from organic wastes was investigated in order to study the effect of pyrolysis

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conditions such as temperature, heating rate and residence time on the product yields and composition [12,13]. Previous works had shown that high heating rates at temperatures around 500 °C with short residence times enhance the formation of liquid products [14,15]. Unfortunately, many of the oils obtained contain polycyclic aromatic hydrocarbons (PAHs) which are of known carcinogenic or mutagenic activity. Furthermore, an increase in the pyrolysis temperatures (above 700 °C), produces oils with a high concentration of PAHs [16,17]. For this reason, the use of these oils as fuel should be limited. However, in some cases high pyrolysis temperatures are required to obtain a clean solid residue with a minimum volatile content [11] that is more resistant to leaching, a char with a higher surface area [18] or a high concentration of the gas fraction [19]. Therefore, new pyrolysis methods must be developed which allow the use of high temperatures with the minimum production of PAHs.

Microwave heating is considered as an alternative for carrying out the pyrolysis of biomass [20], coal [21], oil shales [22,23] and different organic wastes [24]. These materials are poor receptors of microwave energy with which it is impossible to achieve the temperature necessary to complete pyrolysis. However, microwave-induced pyrolysis is possible if the raw material is mixed with an effective receptor [25]. In this work was studied the pyrolysis of sewage sludges by microwave and conventional heating. The objective was to evaluate the chemical characteristics of the oils produced, to compare the results obtained by both methods and to understand the physico-chemical mechanisms involved in pyrolysis. A gas chromatography–mass spectrometry (GC–MS) study was made of the compounds present

in the pyrolysis oils. In addition, certain specific relations between sludge treatment conditions and the composition of the oil were established.

2. Experimental

2.1. Sewage sludges

Four sewage sludges were used: three of them from urban waste water treatment plants (V, B and L) and one from a milk-derivative factory (A). Sludges V, A and B were subjected to aerobic digestion, while sludge L was digested anaerobically. Sludge B was stabilized by the addition of lime and FeCl₃, and sludge A was subjected to conditioning with an organic polyelectrolyte. Finally, mechanical dewatering was carried out, using a filter press (B, A) or centrifugation (V, L).

Table 1 summarizes the main chemical characteristics of the sewage sludges. The volatile matter content (VM) was calculated by heating the sample up to 900 °C in the absence of oxygen while the amount of ashes was determined by burning the sample at 815 °C in a muffle furnace fed with air. It was found that all the sludges had a moisture content higher than 70 wt.% and a relatively high inorganic matter content, sample B having the highest value content, due to its stabilization with lime and FeCl₃, and sample A the highest organic matter content. The composition of the metallic elements present in the inorganic fraction of the sludges is given in Tables 2 and 3. The high moisture content makes that an important amount of water has to be dried off from the sample before the start of pyrolysis. On the other hand, more than 50 wt.% of the dry sludges

Table 1
Selected chemical characteristics of the sewage sludges

	MC (wt.%)	Ashes ⁽¹⁾ (wt.%)	VM ⁽¹⁾ (wt.%)	CV ⁽¹⁾ (kJ/kg)	Organic fraction ⁽²⁾					
					C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O ⁽³⁾ (wt.%)	H/C atomic
V	71.0	31.2	62.3	16 682	52.3	8.0	6.7	0.7	32.3	1.83
L	81.0	38.1	54.7	14 032	49.1	7.3	8.1	1.5	34.0	1.78
B	74.7	42.3	55.9	10 287	39.3	7.3	6.2	0.8	46.3	2.22
A	84.3	17.6	73.2	18 104	47.8	6.7	9.0	1.2	35.4	1.68

MC: Moisture content; VM: volatile matter content; CV calorific value; (1) dry base, (2) dry and ash free base, (3) calculated by difference.

Table 2

Main inorganic element composition of the sewage sludges (expressed as wt.% of metal oxides on a dry base)

	Na ₂ O	MgO	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MnO	SiO ₂	TiO ₂
V	0.28	1.15	4.71	5.97	1.75	0.76	0.04	15.7	0.25
L	0.42	1.49	7.34	5.29	2.98	0.97	0.05	18.9	0.36
B	0.21	1.15	3.05	21.1	8.10	0.05	0.07	6.40	0.16
A	0.80	1.13	0.81	11.0	0.21	0.51	0.01	1.62	0.02

Table 3

Trace elements of the sewage sludge

	Co (ppm)	Cr (ppm)	Pb (ppm)	Mn (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Cd (ppb)	Hg (ppb)
V	3.5	121	246	214	13.2	143	662	9900	2906	919
L	5.0	163	117	239	42.7	192	1020	17 400	1355	1446
B	1.9	30.2	30.7	380	9.2	72.6	215	49 700	<300	570
A	1	19.3	9.6	21.8	7.2	65.3	154	925	5733	357

corresponded to the organic fraction which makes this sludges an interesting source of organic compounds when they are subjected to pyrolysis.

2.2. Microwave-assisted pyrolysis

The drying and pyrolysis of the sewage sludges was carried out in a single process using a multimode microwave cavity oven (M) [26,27]. The experiments were carried out by placing samples of the wet sludge (ca. 15 g) in a quartz reactor, which in

turn was placed inside a multimode resonant microwave cavity. The microwave treatments consisted of subjecting the samples to microwave action for about 6 min. In order to maintain an inert atmosphere during the treatments, a He flow of 200 ml/min was passed through the sample bed for 30 min prior to the commencement of the experiment, this being reduced during the experiment to 10 ml/min. A constant input power of 1000 W was used and the microwave frequency was 2450 MHz. A sketch of the experimental device is shown in Fig. 1. In a

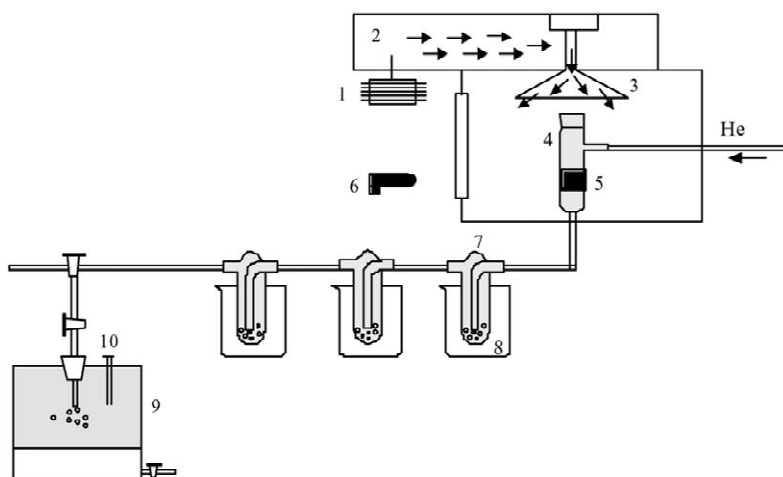


Fig. 1. Schematic diagram of the microwave pyrolysis reactor. 1-magnetron, 2-waveguide, 3-mode stirrer, 4-quartz reactor, 5-sample, 6-optical pyrometer, 7-condenser with dichloromethane, 8-ice bath, 9-gas container, 10-gas sampling.

previous report [25] we showed, that when using microwaves, wet sewage sludge cannot be heated above 200 °C. In order to overcome this problem and to reach the high temperatures required for pyrolysis, the sewage sludge (poor microwave absorber) was mixed with a dielectric material (microwave receptor) that was able to absorb the microwave energy to a larger extent than the wet sewage sludge. Thus, amounts between 0.5 and 3 g of pure graphite—small 3×3 mm strips of graphoil, which were easy to separate from the solid residue obtained after pyrolysis—were used as a microwave receptor. The graphoil was homogeneously blended with the sewage sludge, and the mixture was subjected to microwave action. The temperature of the sample during the experiments was monitored by means of an infrared optical pyrometer. Thermocouples cannot be used under these experimental conditions since arching is generated between the tip of the thermocouple and the graphite, making it impossible to record the temperature. Moreover, accurate measurement of the evolution of the temperature during the process is very difficult for the following reasons. Firstly, there are inherent difficulties in the measurement of the temperature in microwave devices [27]. Secondly, some of the volatiles evolved during pyrolysis may condense on “cold” zones of the walls of the quartz reactor making them dim. This filters the radiation produced by the sample, making the measurement with the optical pyrometer difficult. Finally, the temperature, especially at the beginning of the pyrolysis process, is not uniform throughout the sample due to arching and the formation of “pseudoplasmas” that give rise to hot spots. Despite these difficulties the evolution of the temperature was followed in several experiments (four to six experiments depending on the sample) using the optical pyrometer. The maximum temperatures and heating rates have been averaged and are summarized in Table 4. The results are representative of the maximum temperature and heating rate reached during a given pyrolysis process, but variations of up to ±50 °C in maximum temperature were found for different experiments with the same sample. These variations are to be attributed to the above mentioned difficulties in measuring the temperature and not to a lack of repetition of the experiments (note that the characteristics of the pyrolysis products were quite

Table 4
Maximum average temperature (T_{\max}) and heating rate (R) during the microwave-assisted pyrolysis experiments

	T_{\max} (°C)	R (°C/min)
V	1000	200
L	800	200
B	1000	167
A	1200	300

reproducible). The duration of all the experiments was about 6 min, at the end of which no appreciable gas evolution was observed.

2.3. Electric furnace pyrolysis

For comparative purposes sample V was also pyrolysed in an electric furnace (EF) using a similar quartz reactor but without graphoil. The reaction proceeded in a helium atmosphere with a flow of 15 ml/min. The pyrolysis temperature was 1000 °C and the soaking time was 10 min. The reactor was heated to 1000 °C in approximately 14 min by using the maximum delivered power of the furnace.

2.4. Recovery and characterization of oils

Fig. 1 shows a sketch of the experimental set-up used for collecting the pyrolysis oils (the same collecting set-up was used in the case of the electric furnace pyrolysis). The volatiles evolved from the sample passed through three consecutive condensers containing dichloromethane and were placed in an ice bath. The aqueous fraction recovered in the condensers was then separated from the organic fraction by decantation. An analysis of the aqueous fraction (mostly water) was outside the scope of this paper. Next, the organic fraction dissolved in dichloromethane was dried using anhydrous sodium sulfate and then filtered. Approximately, 5 ml of the clear solution was evaporated at room temperature to near-dryness and then analysed by GC–MS using a Hewlett-Packard HP 6890 gas chromatograph coupled to a HP 5973 quadrupole detector. The gas chromatograph was equipped with a 60 m×0.25 mm capillary column coated with a 0.25 μm thick film of 5% phenyl–methylpolysiloxane (HP-5). Helium was employed as a carrier gas at a constant flow of 0.9 ml/min. The initial oven temperature was 40 °C held

for 5 min and then programmed from 40 to 300 °C at 5 °C/min with an isothermal held for 30 min. Splitless injection was carried out at 300 °C and the purge valve was on at 1 min. The ion source and transfer line temperatures were 230 and 325 °C, respectively. Data were acquired in the full-scan mode between m/z 33–533 and a solvent delay of 6 min was used. Chromatographic peaks were identified by means of NIST mass spectral data library and from their retention times using standard compounds when available. The percentage of the peaks was calculated from the TIC (total ion chromatogram) peak area.

3. Results and discussion

The elemental composition (moisture and ash free), proximate analysis, H/C ratio and calorific value of the sewage sludges are given in Table 1. The results show a high concentration of organic oxygen for all sewage sludges studied, with values ranging between 32 and 46% and a high carbon content with values around of 50%, except for B which has a value of 39.3%. The high values obtained for the H/C atomic ratio are indicative of the strong aliphatic character of these wastes, suggesting the presence of long chains with CH_2 groups. These values are higher than those found for other wastes such as wood and rice husks with values near to 1.4 [17] similar to the H/C values of biomass (1.6–1.7) [10].

The calorific values (CVs) of the sewage sludge were found to be between 14 000 and 18 000 kJ/kg except for sludge B which presents the lowest value. This can be attributed both to its high ash content and its organic composition. Sludge B has the lowest and the highest carbon and oxygen content, respectively. However, the hydrogen percentage is similar to the other samples (~7%). Other wastes such as plastics, wood, paper, rags and garbage present CVs in the range of 17 600 to 20 000 kJ/kg while coal has a CV between 14 600 and 26 700 kJ/kg [28].

Table 5 shows the char, oil and gas yields resulting from the pyrolysis of the different sewage sludges in an M. The yields of the fractions for sludge V, pyrolyzed in an EF, are also included. It is known that high heating rates at temperatures

Table 5
Product yields (wt.%, db) from the pyrolysis of the sewage sludge

	Char	Oil	Gases
Microwave oven			
V	34.8	10.3	54.9
L	43.7	13.1	43.2
B	49.41	4.7	46.15
A	22.9	19.7	57.3
Electrical furnace			
VEF	35.9	3.1	61.0

db=Dry basis.

>650 °C tend to favour the formation of gaseous products at the expense of liquids. These pyrolysis conditions are typical of microwave heating. Attempts were made to reproduce them in the EF (by using the maximum heating rate possible and a pyrolysis temperature of 1000 °C), in order that the results could be compared. As was expected, a high gas yield was obtained in all cases with values ranging from 40 to 57%. Oil represents the smallest fraction with values between 4 and 20% (wt.%, dry basis) depending on the initial sludge and oven used. When pyrolysis was carried out in the EF, the percentage of oil decreased and the gas yield increased with respect to the values obtained in the M. However, there was no significant change in char yield. The increase in gaseous product is thought to have been predominantly due to the secondary cracking of the pyrolysis vapours favoured by the EF. In the electrical furnace the reactor walls remain at higher temperatures than those in the M thereby allowing the volatile products to be subjected to higher temperatures for longer times. The high temperatures reached by the volatiles in the EF favour secondary chemical reactions.

The oil fraction was also analysed for its elemental composition. Table 6 shows the elemental composition of the pyrolysis oils, the H/C ratio and the CV. The pyrolysis oils, after water removal, have a higher carbon content than the initial sludge (see Table 1), and have become strongly deoxygenated. Similar results were found by Pakdel et al. [29] by means of the vacuum pyrolysis of sewage sludge, indicating that many functional groups have been lost during pyrolysis. As a consequence, changes in the overall oxygen content have occurred. On the other hand,

Table 6
Elemental composition, H/C atomic ratio and calorific value (CV) of the pyrolysis oils from the sewage sludge

	C ⁽¹⁾ (wt.%)	H ⁽¹⁾ (wt.%)	N ⁽¹⁾ (wt.%)	S ⁽¹⁾ (wt.%)	O ^{(1),(2)} (wt.%)	H/C	CV (kJ/kg)
VM	73.5	8.5	6.2	–	11.8	1.39	36 813
LM	71.5	8.4	7.5	–	12.6	1.41	35 922
BM	73.2	8.8	6.6	0.59	10.8	1.44	36 178
AM	68.1	9.4	8.4	0.88	13.2	1.66	33 962
VEF	86.5	3.6	4.9	–	5.0	0.50	36 429

(1) Dry base, (2) calculated by difference, M=microwave oven, EF=electrical furnace.

oils have a slightly higher (lower) amount of hydrogen than that of the initial sludge when the M (EF) oven is used. These results give rise to a decrease in the H/C ratio in the oils compared with that of the sludge, indicating a higher degree of aromatisation of the structures present in the oil fraction. This effect is more marked in the EF, where the H/C ratio (~0.5) is similar to that found for highly aromatic carbon materials [30,31].

The CV (moisture free) of the oils reported in this work are higher than those found by other authors [14] from the flash pyrolysis of biomass and somewhat lower than those for light fuel oil [28]. Consequently, the high CV of sewage sludge pyrolysis oils reflects the potential of this fraction for use as liquid fuel.

Besides being used as fuels, the oils may also be an important source of valuable chemical feedstocks. Thus, a study of the composition of pyrolysis oils is essential for assessing their potential in the production of high value products.

Fig. 2 shows the GC–MS chromatograms of the LM, VM, AM and BM oils produced from the pyrolysis of the sewage sludges using a microwave oven. Peak assignments are reported in Table 7.

Pyrolysis oils are complex mixtures made up of hundreds of organic compounds from a wide variety of chemical groups. The compounds identified in the oils have been grouped into the following classes of compounds (see Table 7): *n*-alkanes and 1-alkenes with a number of carbons ranging between C₁₀–C₂₂, monoaromatic compounds, which include benzene and its alkyl derivatives and phenols, PAHs, aromatic nitrogenated compounds, nitrile compounds from paraffins (linear and branched) and from benzene, heavy oxygenated hydrocarbons such as aldehydes (benzaldehyde), carboxylic acids (RCOOH), ketones (RCOR') and esters (RCOOR'), where R and R' are

long aliphatic chains, linear amides, monoterpenes (limonene) and steroids.

In order to determine the distribution of compounds in the pyrolysis oil, a semi-quantitative study was made by means of the percentage of area of the chromatographic peaks. It should be pointed out that these values do not represent the real concentration of the compounds. They serve to show the different composition of the pyrolysis oils. Table 7 shows the values of these proportions for the different types of compounds identified in the LM, BM, VM and AM oils. A high concentration of monoaromatic compounds can be seen for LM and VM. Some of them reach significant proportions, such as toluene with 18.62% for LM and 7.11% for VM and styrene with values of around of 4%. Benzene and xylene have values between 1 and 1.6% for both samples, while alkyl phenols show the highest concentration in the oil derived from sewage sludge B (BM) with 5.36%. All of these compounds are of great importance from an industrial point of view. Toluene, for example, is used in the production of pesticides and solvents, while styrene is one of the most important compounds for making plastic materials, synthetic rubber and polymers. Other researchers have also found considerable amounts of these hydrocarbons in other wastes [16] which shows the importance of pyrolysis in waste treatment for obtaining oils as source of chemicals.

Another important compound from the point of view of the application of the oil as fuel are the aliphatics. Ideally, the compounds in an oil should be straight chain hydrocarbons, as these have a high heating value and lower viscosity. For the oils obtained in this work the total yield of aliphatics (alkanes+alkenes) ranged from 9.29% for sample AM to 16.36% for BM, while the total amount of alkenes was always higher than that of the alkanes. It

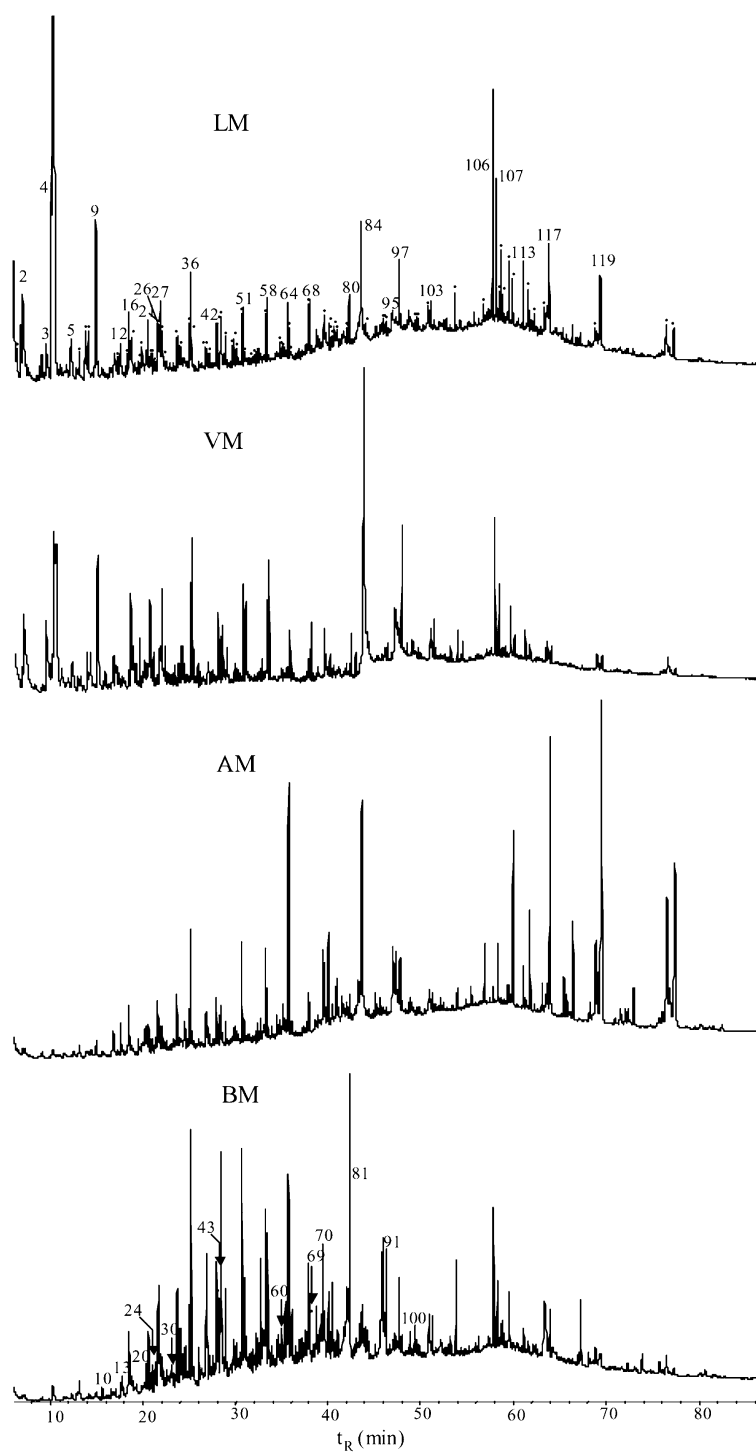


Fig. 2. GC–MS chromatograms of the pyrolysis oils obtained from sewage sludges L, V, A and B using microwave energy (see Table 7 for peak identification).

Table 7

Identification and yield (% area) of the main pyrolysis compounds obtained from sewage sludges L, B,V and A using microwave energy

Peak	Compound	LM	BM	VM	AM
<i>Monoaromatic compounds</i>					
2	Benzene	1.59	–	1.29	–
4	Toluene	18.62	0.39	7.11	+
7	Ethylbenzene	1.12	–	0.91	–
8	Dimethylbenzene	1.23	–	1.13	–
9	Styrene	4.32	+	3.86	0.37
11	Propylbenzene	0.38	–	0.47	+
14	1-Methylethenylbenzene	0.47	–	0.34	–
18	1-Ethenyl-4-methylbenzene	0.17	–	–	–
22	Methylphenol	1.94	0.72	0.93	0.27
26	Methylphenol	+	3.23	+	+
34	Ethylphenol	–	1.41	+	0.76
Σ		29.84	5.75	16.04	1.40
<i>Alkenes</i>					
16	1-Decene	1.41	–	1.81	–
27	1-Undecene	0.83	0.38	1.15	+
35	1-Dodecene	0.34	0.58	0.76	0.34
42	1-Tridecene	0.35	0.83	0.54	0.37
47	Methyltridecene	0.26	0.58	0.21	+
50	1-Tetradecene	0.28	2.02	0.75	0.95
54	Methyltetradecene	+	0.25	–	+
57	1-Pentadecene	0.44	1.48	0.67	0.85
61	Methylpentadecene	0.14	+	+	0.33
64	1-Hexadecene	0.68	1.52	0.35	2.06
67	1-Heptadecene	0.68	1.06	0.4	0.56
72	1-Octadecene	0.26	0.54	0.2	0.84
78	1-Nonadecene	0.22	1.03	+	+
85	1-Eicosene	+	0.52	–	+
87	1-Heneicosene	0.18	–	–	–
98	1-Docosene	0.15	–	–	–
Σ		6.22	10.79	6.84	6.30
<i>Alkanes</i>					
17	Decane	0.83	–	1.22	–
28	Undecane	0.44	+	0.56	+
37	Dodecane	0.35	0.46	0.37	0.23
40	Methyldodecane	0.12	+	0.22	0.14
41	Methyldodecane	0.13	+	+	+
44	Tridecane	0.33	0.59	0.19	0.29
48	Methyltridecane	0.27	0.44	0.13	0.21
49	Methyltridecane	0.21	0.65	0.19	0.21
51	Tetradecane	0.45	0.53	0.5	0.2
55	Methyltetradecane	–	–	–	0.25
58	Pentadecane	0.51	1.24	0.85	0.5
62	Methylpentadecane	0.10	–	+	+
65	Hexadecane	0.47	0.54	0.19	0.13
68	Heptadecane	0.47	0.53	0.39	0.34
73	Octadecane	0.16	0.31	0.15	0.17
79	Nonadecane	0.20	+	+	+
86	Eicosane	0.19	0.28	–	0.32
88	Heneicosane	0.16	–	–	–
99	Docosane	0.11	–	–	–
Σ		5.50	5.57	4.96	2.99

Table 7. Continued

Peak	Compound	LM	BM	VM	AM
<i>Ketones</i>					
10	Methylcyclopentenone	–	0.28	–	–
13	Methylcyclopentenone	–	0.18	–	–
20	Dimethylcyclopentenone	–	0.43	–	–
24	Acetophenone	+	0.35	–	+
30	1-Phenyl-2-propanone	–	0.16	–	–
43	2,3-Dihydro-1H-inden-1-one	–	0.9	+	+
60	Methyltridecanone	–	0.42	–	–
69	2-Pentadecanone	–	0.4	–	–
70	Methylpentadecanone	–	1.33	–	–
81	2-Heptadecanone	–	2.4	–	–
91	2-Nonadecanone	–	0.81	–	–
100	2-Heneicosanone	–	0.29	–	–
Σ			7.95		
<i>Aldehydes</i>					
12	Benzaldehyde	0.95	0.19	–	0.69
<i>Carboxylic acids</i>					
63	Dodecanoic acid	0.24	–	+	0.50
71	Tetradecanoic acid	0.60	–	0.71	1.51
75	Metiltetradecanoic acid	0.28	0.20	–	0.75
76	Metiltetradecanoic acid	0.27	0.28	–	0.70
77	Pentadecanoic acid	–	0.22	–	0.66
84	Hexadecanoic acid	2.96	1.52	10.07	4.80
95	9-Octadecenoic acid	0.84	–	3.20	1.20
96	Octadecanoic acid	–	–	+	1.77
Σ		5.19	2.22	13.98	11.89
<i>Esters</i>					
82	Hexadecanoic acid, methyl ester	–	–	0.19	0.17
94	Octadecanoic acid, methyl ester	–	–	0.32	–
104	Di-(2-ethylhexyl)phthalate	0.34	0.66	0.22	0.16
105	Tetradecanoic acid, dodecyl ester	0.45	–	0.05	0.86
112	Hexadecanoic acid, dodecyl ester	0.58	–	0.30	2.38
116	9-Octadecenoic acid, dodecyl ester	0.45	–	0.31	+
117	Hexadecanoic acid, tetradecyl ester	1.69	0.72	0.26	5.17
118	9-Octadecenoic acid, tetradecyl ester	0.45	0.28	0.33	2.35
119	Hexadecanoic acid, hexadecyl ester	1.7	+	0.3	8.76
120	9-Octadecenoic acid, hexadecyl ester	0.85	0.46	0.41	4.23
121	Hexadecanoic acid, octadecyl ester	0.79	+	0.14	4.96
Σ		7.30	2.12	2.83	29.04
<i>Nitrogenated compounds</i>					
1	Methylpropanonitrile	0.72	–	–	–
6	Methylpentanonitrile	0.5	0.43	–	0.27
15	Benzonitrile	–	+	–	1.15
25	Methylbenzonitrile	+	0.36	–	0.31
29	Methylbenzonitrile	+	0.53	–	0.11
31	Benzeneacetonitrile	0.44	0.38	0.35	0.56
38	Benzenepropanonitrile	0.47	3.14	–	0.38
59	Naphthalencarbonitrile	–	0.5	–	0.25

Table 7. Continued

Peak	Compound	LM	BM	VM	AM
80	Hexadecanonitrile	0.45	–	0.39	0.35
89	Heptadecanonitrile		0.4	0.19	
92	Octadecanonitrile	0.12	+	0.48	–
101	Eicosanonitrile	0.16	–	–	–
3	Pyridine	1.29	–	1.65	–
5	Methylpyridine	1.44	+	1.15	–
39	Quinoline	+	+	0.48	0.30
52	Methyl-1H-indole	0.25	1.19	–	–
97	Hexadecanamide	0.71	0.88	1.29	1.16
102	9-Octadecenamide	0.5	0.45	0.42	0.43
103	Octadecanamide	0.45	0.33	0.37	0.2
Σ		7.50	8.59	6.77	5.47
<i>Polycyclic aromatic hydrocarbons</i>					
21	1H-Indene	0.74	0.63	1.17	0.35
32	Methylindene	0.26	0.69	0.71	–
33	Methylindene	+	0.93	0.29	–
36	Naphthalene	0.99	2.81	1.51	1.27
45	2-Methylnaphthalene	1.44	3.71	1.03	0.84
46	1-Methylnaphthalene	0.45	+	0.42	0.33
53	Vinylnaphthalene	–	0.47	–	–
56	Acenaphthylene	–	1.18	0.22	0.32
66	Fluorene	+	0.26	–	0.22
74	Phenanthrene	0.26	0.93	0.21	0.58
83	4H-Cyclopenta[def]phenanthrene	–	0.66	–	–
90	Fluoranthene	–	0.48	–	–
93	Pyrene	–	0.38	–	–
Σ		4.14	13.13	5.56	3.91
<i>Terpenes and steroids</i>					
19	Limonene	0.34	–	0.74	–
106	3-Cholestene	2.45	1.75	1.7	0.21
107	Cholestene	1.7	0.55	0.66	0.72
108	Cholestene	0.45	+	0.09	–
109	Cholestene	1.00	+	0.17	–
110	Cholestadiene	0.29	0.53	0.10	–
111	Cholestadiene	0.83	+	0.49	+
113	3-Ethylcholestene	0.91	0.28	0.32	+
114	3-Ethylcholestene	0.48	+	0.15	+
115	4-Cholesten-3-one		1.05	–	
Σ		8.45	4.16	4.42	0.93

is worth noting that the L,V and B sewage sludges have a much higher ash content than A, suggesting that some components of char may have a catalytic effect, producing straight chain hydrocarbons. This behavior may be related to the presence of heavy metals and also, in the case of B, to the influence of the calcium oxide added during the stabilization process of the sludge. It is also assumed that CaO

may catalyse secondary reactions of primary pyrolysis products. This effect has already been studied by Tingyu et al. in their work on the pyrolysis of coal [32]. The authors show how CaO can catalyse the cracking of heavy alkanes to light alkanes and the dealkylation of polycyclic aromatic hydrocarbons, increasing the total yield of alkanes. These findings are connected with our results from

the pyrolysis of B. The oil obtained (BM) exhibits the highest proportion of aliphatic compounds mainly due to the high proportion of alkenes originated. This seems to suggest that the dehydrogenation of alkanes to give alkenes may also be due to the catalytic action of CaO.

Most of the oxygenated compounds are long chain aliphatic ketones, acids or esters whose proportions depend on the origin and the form of treatment of the sludge. As can be seen in Fig. 2 and Table 7, the pyrolysis oil BM, obtained from the sludge stabilized with lime (B), is the only one that contains ketones. Alkyl cyclopentenone, aromatic and aliphatic ketones with an odd number of carbon atoms (C_{15} – C_{21}) were observed. The largest proportion of carboxylic acids ranging from C_{12} to C_{18} is to be found in the VM oil which has a high percentage of palmitic acid. As mentioned in the Experimental section, sewage sludge V came from a waste treatment plant and was subjected to aerobic digestion. The sludge from the milk-derivative factory (A) and treated aerobically also produced an oil (AM) with a high proportion of acids. In addition, this oil contains the highest proportion of esters which are mainly derived from the fatty acids palmitic (C_{16}) and oleic (C_{18}) with an alkoxy group (OR) containing long aliphatic chains with a even number of carbon atoms from C_{12} to C_{18} . In contrast, the pyrolysis of the sludge treated anaerobically (L) gives rise to the oil (LM) with the highest proportion of steroids.

Among the nitrogen containing compounds, long chain aliphatic amides, nitriles and polyaromatic nitrogen compounds were observed. The highest and lowest values were obtained for oils BM and AM, respectively.

Another important constituent of the pyrolysis oils from an environmental point of view are the PAHs. The evaluation of these compounds in a fuel is of great importance since some of them have been shown to be carcinogenic and/or mutagenic.

PAHs have been detected by other workers in a variety of biomass and sewage sludge using fixed and fluidised bed reactors with conventional heating [14,16,17,26]. It was observed that the amounts of PAHs when the pyrolysis temperature was $<500\text{ }^{\circ}\text{C}$ were negligible but an important increase in their yields took place when the reactor temperature was increased ($>700\text{ }^{\circ}\text{C}$) [33]. These results indicate that

when high pyrolysis temperatures are required conventional heating will give rise to a toxic oil rich in PAHs.

The most important aromatic hydrocarbons present in the pyrolysis oils from the sewage sludge using microwave radiation are shown in Table 7. The oil from sewage sludge B contains a higher proportion of PAHs (13.13%) than the other oils (approx. 4–6%), with aromatic compounds of up to four rings and a molecular mass of 202, i.e., fluoranthene and pyrene. These compounds were not observed in the other three oils. On the other hand, the oil from A has the lowest concentration of PAHs. It must be noted that sewage sludges B and A have the highest and lowest ash content, respectively.

The bicyclic compounds such as naphthalene and methylnaphthalenes are present in a higher proportion than other PAHs for all the oils studied. It should be pointed out that the high proportion of these compounds in the oil from B may again be associated with the catalytic effect of CaO. This result has also been confirmed by other workers for coal tars. Notably, naphthalene and substituted naphthalene yields increased when calcium oxide was added [31].

The formation of PAHs can be explained by several reaction pathways. A Diels–Alder reaction mechanism has been suggested by several authors [16,17] as responsible for the formation of these compounds. It is assumed that the pyrolysis of alkanes at high temperatures gives rise via dehydrogenation to alkenes and dienes which by cyclisation and subsequent aromatisation produce the aromatic compound [34,35]. The growth of aromatics to higher-molecular-mass compounds might occur via a Diels–Alder reaction, although other ways of formation of PAHs have been also suggested, i.e., direct combination of aromatic rings and/or by H_2 abstraction– C_2H_2 addition [33].

In connection with these models, one possible explanation for the high amount of PAHs in the BM oil might be that in this sample the formation of alkenes, which are precursors of aromatic compounds, is favoured.

However, despite the high temperatures reached using microwave radiation ($\sim 1000\text{ }^{\circ}\text{C}$) the proportion of PAHs was particularly low in the case of LM, VM and AM. Significantly, heavy PAHs such as ben-

zopyrenes, chrysene or benzofluoranthenes, that are biologically active, were not produced.

In order to compare microwave-assisted and “conventional” pyrolysis, sewage sludge V was also pyrolyzed in a fixed bed reactor placed in an electrical furnace working at 1000 °C, as described in the Experimental section. Fig. 3 shows the GC–MS chromatogram of the pyrolysis oil from V (VEF). The identification of the peaks and their percentage in area are given in Table 8. In agreement with the results obtained by other authors discussed above, the oil is composed basically of polyaromatic compounds. Heterocyclic compounds with sulfur such as benzothiophene, dibenzothiophene, and with nitrogen such as quinoline and isoquinoline, were also observed. Other nitrogen compounds such as benzonitrile, methyl benzonitrile and naphthalene carbonitrile and some PAHs with an olefinic group that included indene, acenaphthylene and vinyl naphthalene were also identified. PAHs with up to six rings and with a molecular mass of 276 were also found, i.e., indenepylene, benzo[*ghi*]perylene, and anthanthrene. The concentration of PAHs decreased when the number of rings and the molecular mass increased. Quantitatively, the most important compound analysed was naphthalene (10.95%), although significant proportions of acenaphthylene, phenanthrene, fluoranthene, benzo[*a*]anthracene, benzofluoranthenes ($[j]+[b]$) and benzo[*a*]pyrene were observed. The total percentage of polycyclic aromatic compounds identified was 77.91%. By contrast, these

compounds were not produced in the case of the microwave-assisted pyrolysis of sample V.

The results above show that oils resulting from microwave pyrolysis are more aliphatic and oxygenated than those produced by conventional heating at the same temperature (1000 °C). Secondary reactions take place to a higher extent during conventional heating giving rise to the formation of PAHs. This is due to the fact that in microwave pyrolysis the sample is heated directly so that it reaches a high temperature in a very short time while the reactor walls remain at a lower temperature than the bulk of the sample. Under these conditions the residence time of the volatiles in the hot zone is relatively short, which does not favour secondary reactions. In conventional heating the heat flow comes from the walls of the reactor so the temperature is higher in the reactor than inside the bulk of the sample. The volatiles therefore have a longer residence time at high temperatures than in the microwave oven, which gives rise to more favourable conditions for the formation of PAHs.

4. Conclusions

Sewage sludge pyrolysis can be achieved by microwave assisted pyrolysis using graphite as microwave absorber. Temperatures of up to 1000 °C were reached. The pyrolysis oils obtained have a high calorific value and a low proportion of com-

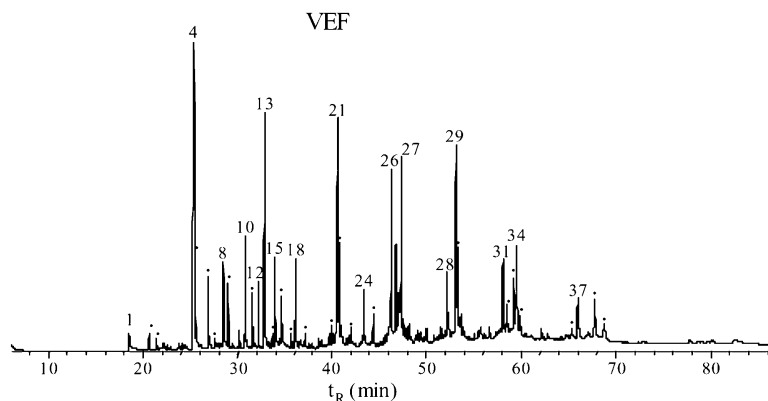


Fig. 3. GC–MS chromatogram of the pyrolysis oil obtained from sewage sludge V using an electric furnace (see Table 8 for peak identification).

Table 8
Identification and yield (% area) of the main pyrolysis compounds obtained from V sample using an electrical furnace

Peak	Compound	% Area
1	Benzonitrile	0.58
2	Indene	0.26
3	Methylbenzonitrile	0.20
4	Naphthalene	10.95
5	Benzo[thiophene]	1.65
6	Quinoline	1.67
7	Isoquinoline	0.42
8	2-Methylnaphthalene	1.61
9	1-Methylnaphthalene	0.92
10	Biphenyl	1.7
11	Biphenylene	0.91
12	Vinylnaphthalene	1.12
13	Acenaphthylene	7.11
14	Acenaphthene	0.21
15	Naphthalencarbonitrile	1.97
16	Naphthalencarbonitrile	1.45
17	Phenalene	0.22
18	Fluorene	2.02
19	Methylfluorene	0.27
20	Dibenzothiophene	0.33
21	Phenanthrene	6.10
22	Anthracene	1.92
23	Phenylnaphthalene	0.29
24	4H-Cyclopenta[def]fenantreno	1.11
25	Phenylnaphthalene	0.66
26	Fluoranthene	5.35
27	Pyrene	5.81
28	Benzo[ghi]fluoranthene	1.49
29	Benzo[a]anthracene	4.51
30	Chrysene	2.03
31	Benzo[j]+benzo[b]fluoranthene	3.15
32	Benzo[k]fluoranteno	0.83
33	Benzo[e]pyreno	1.43
34	Benzo[a]pyreno	3.04
35	Perylene	0.67
36	Dibenzoanthracene	0.31
37	Indenopyrene	1.70
38	Benzo[ghi]perylene	1.30
39	Anthanthrene	0.64
Σ		77.91

pounds of considerable environmental concern such as PAHs. Conversely, heating the sludge to high temperatures using conventional methods gives rise to an oil rich in PAHs. Depending on the type of sludge, the oil produced by microwave heating has a high proportion of long chain aliphatic hydrocarbons which is of significance for its use as fuel. CaO seems to catalyze the formation of aliphatic com-

pounds and to some extent also aromatic compounds. Some important chemicals from an industrial point of view, have also been obtained in a high proportion. These include benzene, toluene and styrene. The other compounds present in the oil contain long aliphatic chains that can be converted to aliphatic hydrocarbons with a high heating value.

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