

# Characterisation of products from pyrolysis of waste sludges

Tamer Karayildirim<sup>a</sup>, Jale Yanik<sup>a,\*</sup>, Mithat Yuksel<sup>b</sup>, Henning Bockhorn<sup>c</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Ege University, 35100 Izmir, Turkey

<sup>b</sup> Department of Chemical Engineering, Faculty of Engineering, Ege University, 35100 Izmir, Turkey

<sup>c</sup> Institut für Chemische Technik, Universität Karlsruhe (TH), 76131 Karlsruhe, Germany

Received 30 April 2005; received in revised form 29 November 2005; accepted 1 December 2005

Available online 6 January 2006

## Abstract

The pyrolysis of waste sludges was investigated using thermogravimetry/mass spectrometry (TG/MS) and a fixed-bed reactor. Two types of sludge were used, namely mixed sludge and oil sludge. In TGA/MS measurements, two degradation steps were observed. Degradation of organic structures, in sludge took place in the first step, while inorganic materials in sludge were mainly decomposed in a second step (above 500 °C). In a fixed-bed reactor, the catalytic effect of inorganic matter in addition to organic matter was monitored the quality and yield of products from pyrolysis. Pyrolysis of oil sludge produced a larger amount of oil containing more aliphatic compounds and a high calorific value. On the other hand, pyrolysis of mixed sludge gave a smaller amount of oil being rich in polar compounds. The gaseous products from pyrolysis consist of high amount of combustible gases. Landfilling was found to be the best alternative to dispose off the pyrolytic char obtained from pyrolysis.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Oil sludge; Waste sludge; Pyrolysis

## 1. Introduction

The management of sewage sludge in an economically and environmentally acceptable manner is one of the critical issues facing society today. In fact, the amount of sludges produced by wastewater treatment plants is going to dramatically increase in both industrialized and emerging countries. Recycling to agriculture (landspreading), incineration or landfilling are the most common disposal routes [1]. However, landspreading leads to an increase in concentration of heavy metals in the soils and indirect emissions into air and water. Disposal by landfilling requires a lot of space and poses a potential environmental hazard. On the other hand, although incineration can provide a large volume reduction and energy recovery, it generates emissions into the air, soil and water.

Several technologies presenting an alternative to conventional combustion processes are currently being developed. These technologies mainly include the wet oxidation process, pyrolysis and the gasification process. Pyrolysis has significant advantages over the other methods. Pyrolysis produces more

useful products; gas, oil and solid char which may be used as fuels or a feedstock for petrochemicals and other applications. In addition, heavy metals (except mercury and cadmium) could be safely enclosed in the solid char. Pyrolysis of sewage sludge under different conditions has been studied to investigate the pyrolysis mechanism and to characterize the gases, oils and solid char.

Due to the advantages of pyrolysis, in this study, pyrolysis of two different types of sludge was carried out in a fixed-bed reactor. The main goal of this study was to characterize the composition of gas and liquid products obtained from pyrolysis to determine their utilization area. To understand the thermal behaviour of sludges during pyrolysis, thermogravimetric analysis was also performed.

At present, one of the sludges used in this study is disposed of by incineration, the other is disposed off by landfilling.

## 2. Materials and methods

### 2.1. Materials

In this study, two different kinds of sludge were used. One of them consisted of a filtrated cake of mixed chemical and activated sludge from the waste water-treatment plant of a Petrochemical Industry, PETKIM-Izmir. The other sludge was a oily sludge, sampled from the primary decanting step following API separation in the waste water-treatment plant

\* Corresponding author. Tel.: +90 232 388 4000x2386; fax: +90 232 388 8264.

E-mail address: [jale.yanik@ege.edu.tr](mailto:jale.yanik@ege.edu.tr) (J. Yanik).

Table 1  
Proximate analysis of sludges (wt%)

	Moisture	Ash	Volatile matter
MS	2.4	20.7	55.0
OS	26.3	31.6	31.7

of a refinery in Izmir. Mixed sludge (MS) was initially dried under atmospheric conditions to constant mass and the dried sludge was then ground to approximately 1 mm in diameter particles. Oil sludge (OS) was used as received. Table 1 shows some properties of sludges. Inorganic constituents of sludges are given in Table 2. Oil sludge had a relatively low volatile matter content because of its elevated moisture and ash content.

## 2.2. Experimental procedures

### 2.2.1. TG-MS

Thermogravimetric experiments were carried out with a thermobalance coupled to a quadrupole mass spectrometer [2]. Pure helium was used as purge gas. The flow rate of the purge gas was approximately  $100 \text{ cm}^3 \text{ min}^{-1}$ . Runs were performed at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  using a sample amount of 10–20 mg. The quadrupole mass spectrometer (Balzers-QMG 420) was connected to the thermo balance via an open coupling with a differential pressure reduction via a platinum orifice. The coupling could be heated up to  $500 \text{ }^\circ\text{C}$  to prevent condensation of the evolved products. The high pressure and the coupling was located directly above the heated sludge sample. Part of the probed gases was pumped behind the orifice before entering the low pressure section of the coupling. The low pressure end of the coupling was inserted directly into the ion source of the mass spectrometer. The ionizing voltage of the cross-beam electron impact ionization source amounted to 30 eV.

In thermogravimetric analysis, the percentage of mass loss was calculated according to the equation below

$$\text{Weight loss (\%)} = \left( \frac{(m_i - m_a)}{m_i} \right) 100$$

where  $m_i$  is the initial mass (g);  $m_a$  is the actual mass (g).

### 2.2.2. Pyrolysis procedure

The pyrolysis experiments were performed in a fixed bed design and stainless steel reactor ( $L$ ; 210 mm;  $\varnothing$ ; 60 mm) under atmospheric pressure using a semi-batch operation. In a typical pyrolysis experiment, a quantity of 140 ( $\pm 0.5$ ) g of sludge was loaded and then the reactor temperature was increased at a heating rate of  $7 \text{ }^\circ\text{C min}^{-1}$  up to  $500 \text{ }^\circ\text{C}$  and held at this temperature for 1 h. The nitrogen gas ( $25 \text{ mL min}^{-1}$ ) swept the volatile products from the reactor into the traps. Following the

condensation (in the first two traps by cooling with ice bath), non-condensable volatiles passed through a lead nitrate solution (33 wt%) containing traps to absorb  $\text{H}_2\text{S}$  and then the remaining gases were collected in Tedlar plastic bags.

After the reaction, the aqueous phase in the condensate was separated from the organic phase (pyrolytic oil) by centrifugation. In each experiment, char, pyrolytic oil (oil) and aqueous fraction yields were determined by weight and the gas fraction yield was calculated by weight difference.

## 2.3. Gas analyses

Pyrolysis gases collected in Tedlar bags were analyzed by gas chromatography using a HP model 5890 series II with a thermal conductivity detector. A stainless steel packed column ( $6.0 \text{ m} \times 1/8 \text{ in. Propack Q}$ ,  $2.0 \text{ m} \times 1/8 \text{ in. 5A}$  molecular sieve, serially connected to each other) was used. The separation of  $\text{CO}_2$ ,  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$  and  $\text{C}_6$  hydrocarbons was achieved by the Propack Q column and the separation of  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{CO}$  was carried out with the MS 5A column.

The amount of hydrogen sulphur in the gaseous products was determined as a lead sulphur precipitate, which was formed from the reaction between  $\text{H}_2\text{S}$  and lead nitrate in the traps. The lead sulphur precipitate was filtered, washed with distilled water, dried at  $110 \text{ }^\circ\text{C}$  and weighed.

## 2.4. Oil analysis

Pyrolytic oils obtained under the same conditions were well mixed and homogenized prior to analysis being made. The viscosity and calorific value of pyrolytic oils were determined according to some physical properties of pyrolytic oils were determined by using the following standard methods; ASTM D445 and ASTM D240. Elemental analysis (C, H, and N) of oils was determined with an elemental analyzer (Carlo Erba 1106). The Sulphur amount in pyrolytic oils was determined using Ultraviolet Fluorescence according to ASTM D5453.

The asphaltenes of the pyrolytic oils were precipitated by addition of *n*-hexane. Soluble (in *n*-hexane) oil portions were fractionated by column chromatography into aliphatic, aromatic and polar fractions using hexane, toluene and methanol, respectively [3]. Aromatic and polar fractions were subjected to IR analysis.

The aliphatic fractions were analyzed for different boiling points by GC-FID, according to the standard test method for boiling range distribution of petroleum fractions (ASTM D 2887). Identification of compounds from the aliphatic fraction of pyrolytic oils was carried out using a gas chromatograph equipped with a mass selective detector (column, HP-1; cross-linked methyl siloxane,  $25 \times 0.32 \text{ mm} \times 0.17 \text{ } \mu\text{m}$ ; temperature

Table 2  
Main inorganic elements of the sludges (expressed as mg/kg sludge, on dry basis)

	Fe	Cu	Cr	Zn	Co	Ni	Ca	Mg	Na	K	N
MS	3900	14	7	500	77	75	6700	4250	7920	2670	63,600
OS	43,826	590	427	4206	26	631	17,775	6038	2958	83,487	nil

program, 40 °C (hold 10 min) → 300 °C (rate 5 °C min<sup>-1</sup>) hold for 10 min). Compounds were identified by means of the Wiley library-HP G1035A and NIST library of mass spectra and subsets HP G1033A.

### 2.5. Characterization of pyrolytic carbons

The structural characterization of the pyrolytic carbons was carried out by physical adsorption of N<sub>2</sub> at -196 °C. The adsorption isotherms were determined using a automatic SORPTION 1990. The surface area was calculated using the BET equation.

## 3. Results and discussion

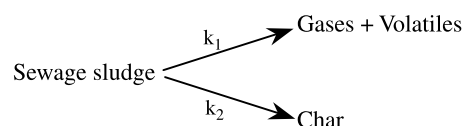
### 3.1. Thermogravimetry results

Thermogravimetric analysis provides a prior knowledge of initial and final temperatures for thermal degradation of sludge. The results of TGA/DTG are shown in Fig. 1. Pyrolysis of sludges took place in two stages. For MS, the most abundant release of volatile matter was observed in the temperature range 200–500 °C. In this temperature range, two different

peaks are observed in the DTG curve. The first peak might be due to decomposition and devolatilization of less complex organic structures which is a small fraction. The second peak was caused by decomposition of more complex organic structures corresponding to a larger fraction. In the case of OS, the main decomposition peak was observed between 100 and 350 °C. This is reasonable because oil sludge consisted of petroleum hydrocarbons with a wide range in boiling point. Evaluation of water and hydrocarbons took place simultaneously. In the second stage of sludge pyrolysis, mainly decomposition of inorganic materials took place.

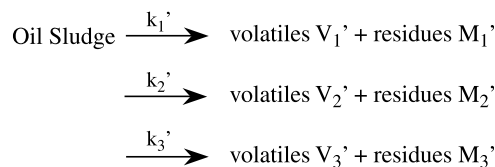
The reaction scheme of sludge pyrolysis is very complex. Various models for pyrolysis of sludge have been reported [4–7]. However, there is not a single model which describes the pyrolysis of a wide variety of sewage sludge successfully.

Ahuja et al. [6] has proposed the following global reaction scheme for pyrolysis of sewage sludge.



The model has accounted for the competition between the char formation reactions and the weight loss reactions since the activation energies for both reactions were quite close.

On the other hand Shie et al. [7] have proposed a three-reaction model to present the pyrolysis of oil sludge as follows;



It was concluded [8] that the individual extents and amounts of products of three reactions were temperature dependent. Thus, the pyrolysis processes before 350 °C would include physical volatilization with the transformation reaction (the first reaction of the three-reaction model), while above 440 °C, the reaction mechanism includes the other two reactions of the three-reaction model.

The weight losses in the first step are about 56 wt% for MO and 50 wt% for OS. At the final pyrolysis temperature (900 °C), the residue percent of MO and SO are about 34 and 38 wt%, respectively. Although, the ash content of OS was higher than that of MS, the residue amount from both pyrolysis of MS and OS were close. It may be concluded that the amount of final residue depends on the organic materials in sludge as well as the amount of inorganic materials.

### 3.2. TG/MS results

It has been established that TG/MS is well suited for the characterization of gaseous thermal degradation products of different materials [9–12]. To identify the degradation products from pyrolysis of sludge by TGA, thermogravimetric experiments were carried out with a thermobalance coupled to a

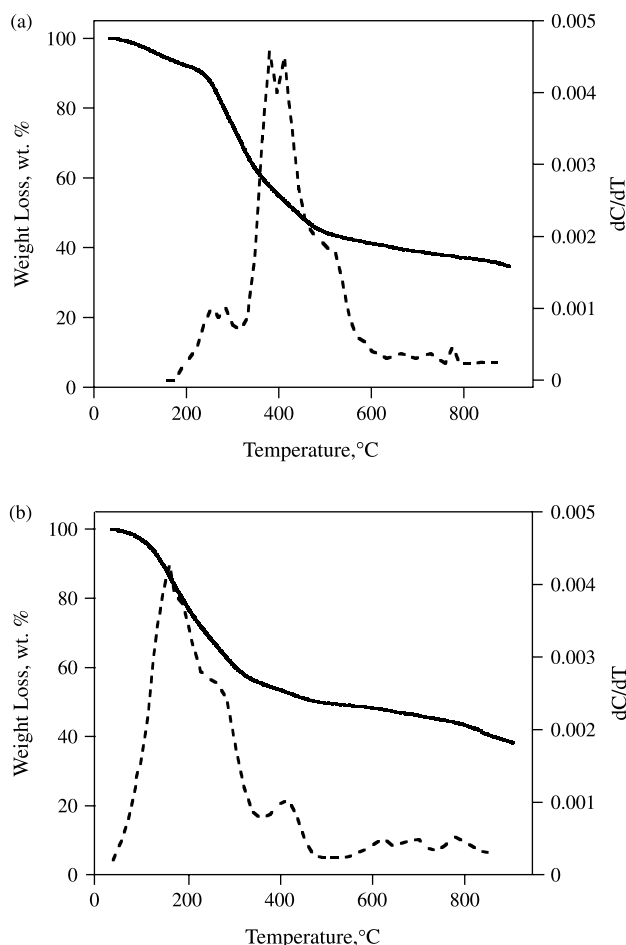


Fig. 1. TG and DTG curves of sludges at the heating rate of 10 °C min<sup>-1</sup>. (a) Mixed sludge; (b) oil sludge.

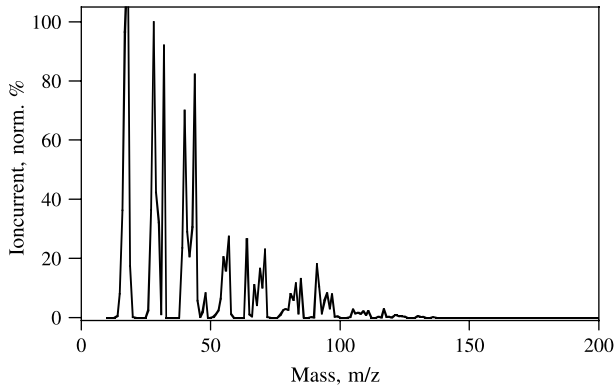


Fig. 2. Mass spectrum obtained by pyrolysis of MS.

quadrupole mass spectrometer. Fig. 2 shows a representative mass spectrum and Fig. 3 illustrates some of the most relevant peaks obtained in the TGA degradation of S-1.

Methane ( $m/z=16$ ) evolution starts at low

temperatures. The maximum evolution rate is observed between the temperatures of 400–550 °C and the evolution continues over 550 °C because of the breaking of terminal C–C bonds in the condensed organic structure in coke. Water ( $m/z=18$ ) evolution up to 200 °C is due to the releasing of free and physically bonded water. In the temperature range 200–600 °C, dehydration reactions and decomposition of crystal water are responsible for water evolution. Over 600 °C, water may be generated from the degradation of oxygen containing high molecular weight organic compounds by the catalytic effect of inorganic materials.

The main hydrocarbons ( $m/z=27, 43, 56$ ) from the decomposition of organic compounds involve in the temperature range of 250–550 °C. For  $m/z=30$ , both  $C_2H_6$  and NO might be assigned. By considering the shape of the evolution curve, it might be said that up to 500 °C  $C_2H_6$  evolved, whereas above 500 °C NO was formed from the

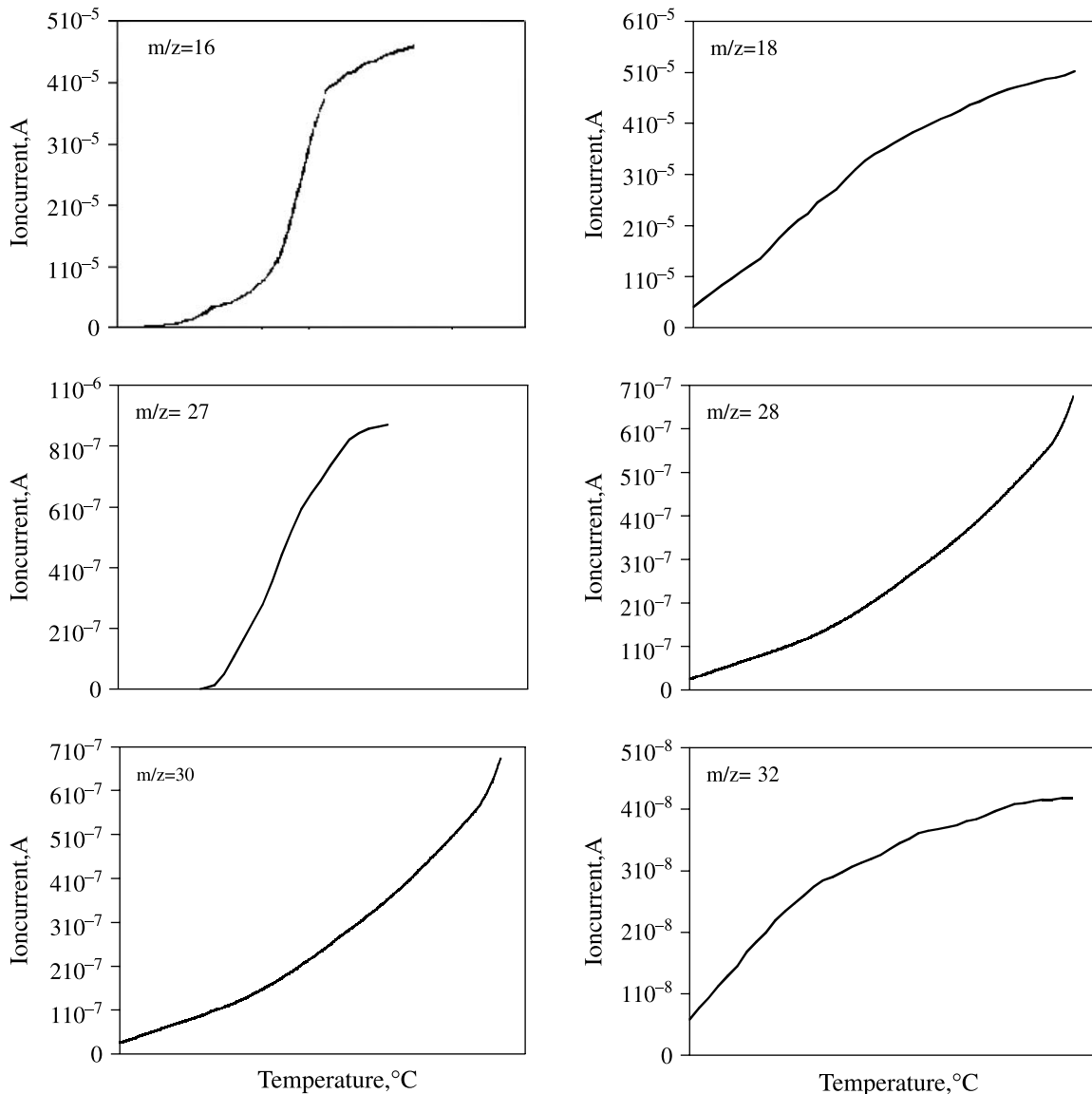


Fig. 3. Evolution profiles of the pyrolysis products of MS.

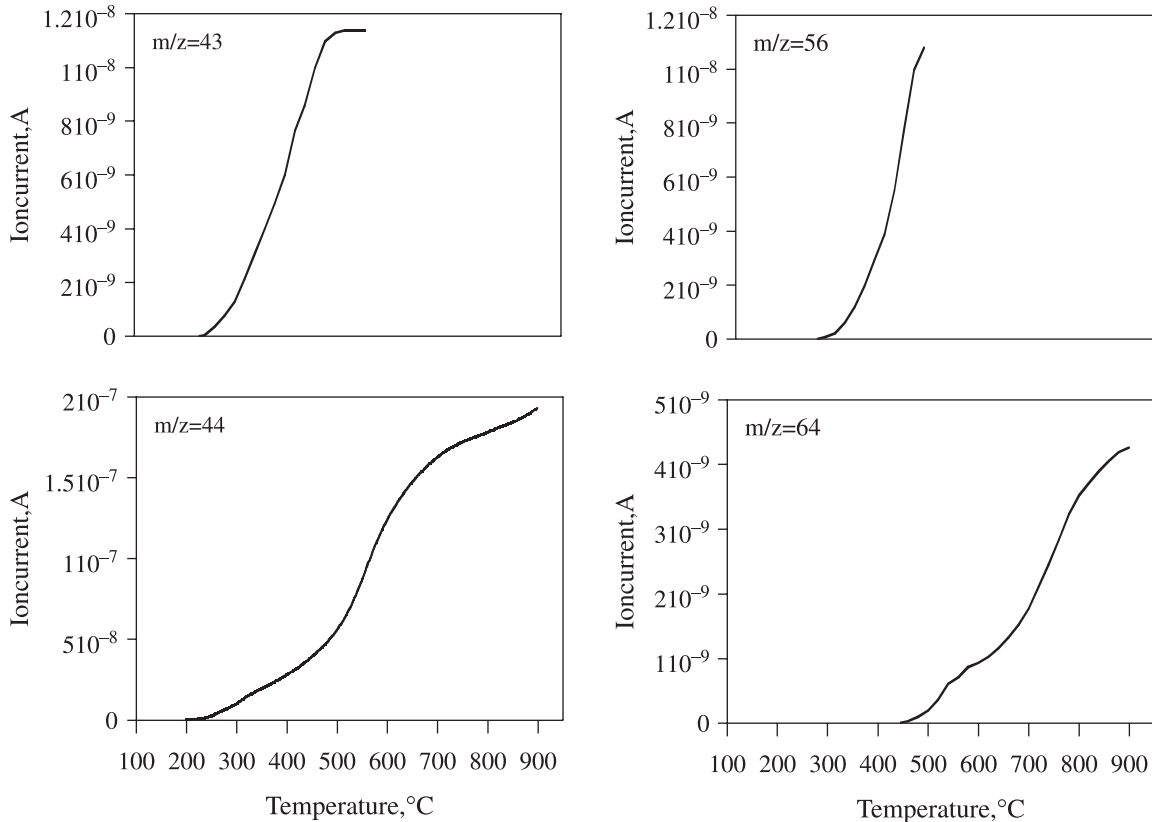
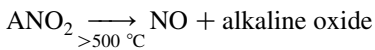
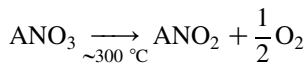


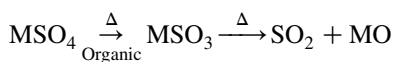
Fig. 3 (continued)

degradation of alkaline nitrates according to the following reactions



Both methanol and methyl ammonium compounds may be considered for  $m/z=32$ . Up to 400 °C methanol is formed from the degradation of organic compounds in sludge. At higher temperatures, the degradation of nitrogen containing cyclic compounds in coke may produce methyl ammonium compounds.

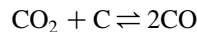
The  $\text{SO}_2$  ( $m/z=64$ ) evolution was observed at 450 °C and might be due to the degradation of inorganic sulphides and sulphates according to the following equation.



Because of the presence of oxygenated organic compounds, sulphate can be reduced to sulphite instead of sulphur.

The formations of CO ( $m/z=28$ ) and  $\text{CO}_2$  ( $m/z=44$ ) up to 600 °C were generated from the degradation of organic compounds. At higher temperatures, decompositions of carbonates lead to the formation of carbon dioxide and at

these temperatures carbonmonoxide was formed according to the Boudouard reaction.



On the other hand, degradation of OS produced more compounds in number than MS pyrolysis (Fig. 4). As in the case of MS, the evolution profiles of  $m/z=16, 17, 18, 28, 32, 44$  and 64 have also been monitored in the degradation of OS and the shape of the evolution profiles of these mass numbers were similar

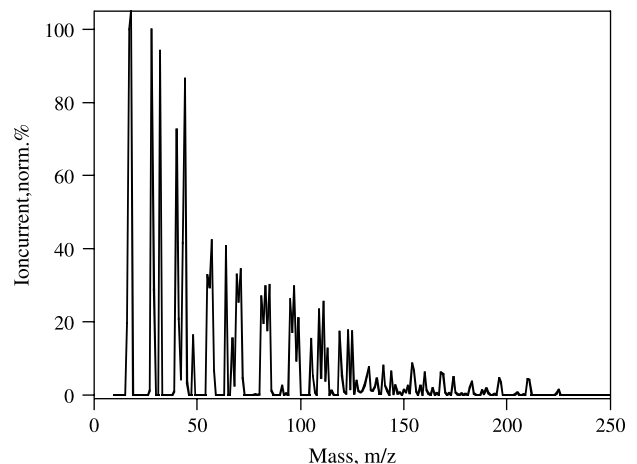


Fig. 4. Mass spectrum obtained by pyrolysis of OS.



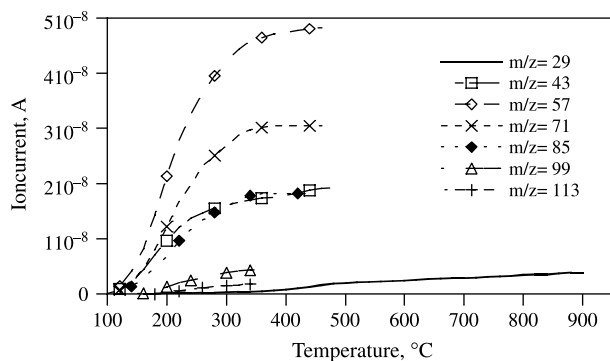


Fig. 5. Evolution profiles of hydrocarbons from the pyrolysis of MS.

to that of MO. Thus, the explanation of the evolution profiles for MS is also valid for the same degradation products of OS.

The other compounds ( $m/z=29$  ( $C_2H_5$ , -ethyl), 40 ( $C_3H_4$ , propyne), 43 ( $C_3H_7$ , -propyl), 57 ( $C_4H_9$ , -butyl), 70 ( $C_5H_{10}$ , pentene), 71 ( $C_5H_{11}$ , -pentyl), 85 ( $C_6H_{13}$ , -hexyl), 99 ( $C_7H_{15}$ , -heptyl) and 113 ( $C_8H_{17}$ , -octyl)) are mainly hydrocarbons. All hydrocarbons, except  $m/z$  29 and 40, are formed in the temperature range of 100–460 °C (Fig. 5). As known, in this temperature range decomposition of organic structure takes place. However, for the  $m/z$  29 and 40, evolutions were observed up to 900 °C. The evolution of  $C_3H_4$  ( $m/z=40$ ) at high temperatures might be the result of breaking of the coke structure. On the other hand, for  $m/z=29$  both  $C_2H_5$  and  $CHO^+$  might be assigned. By considering the shape of the evolution curve, it might be said that up to 460 °C,  $C_2H_5$  evolved, but above 460 °C,  $CHO^+$  was formed from the degradation of polycondensed compound which is present in coke.

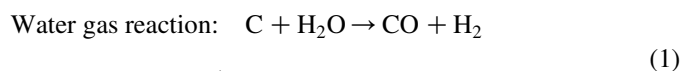
### 3.3. Pyrolysis of sludges in fixed-bed reactor

The pyrolysis of sludges in the fixed-bed reactor was carried out at 500 °C. The pyrolysis temperature has been estimated based on the results obtained by TGA. The temperature used is in good agreement with the literature. Chang et al. [13] reported that the pyrolytic reaction of oil sludge is significant in the 450–800 K range. In pyrolysis of sewage sludge between 450 and 800 °C, it was found that an increase in the pyrolysis temperature led to a decrease in the solid fraction and to an increase in the gas fraction, while the liquid fraction remains almost constant [14]. In fluidized bed pyrolysis of sewage sludge, the selectivity to tar and oil was the highest around 550 °C [15]. By considering the behavior of the heavy metals during pyrolysis, Stambach [15] proposed that the pyrolysis should be limited to temperatures not much higher than 600 °C.

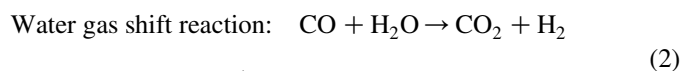
Table 3 shows the char, liquid (aqueous fraction + oil) and gas yield resulting from the pyrolysis of sludges. The results presented in the table include the mean value and the standard deviation of at least three pyrolysis runs carried out at the same temperature.

As expected, the yields change with the type of sludge. The differences between the yields are due to the difference in both the type and the amount of organic component of the sludge as well as the inorganic contents. Pyrolysis of oil sludge produced

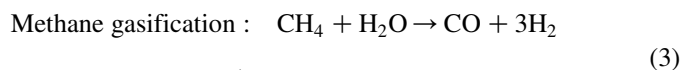
a larger amount of oil than that of mixed sludge. It is noted that although OS contained a larger amount of ash than MS, the char yields from pyrolysis both of MS and OS are similar. This can be explained by considering that the OS contains highly degraded organic compounds that are easy to volatilize, producing lower pyrolysis char. On the other hand, it seems that inorganic constituents in sludge affects the yields of water fraction. The amounts of the aqueous fraction from pyrolysis of MS were much greater than the moisture content of sludge. This is reasonable, because water originates from a dehydration reaction of organic compounds in addition to physically bonded and free water in the sludge [16]. However, in the pyrolysis of OS, the percentage of the aqueous fraction obtained was less than the moisture content of the sewage sludge. This suggests that some of the water is consumed during pyrolysis [17]. The consumption of water may be attributed to the following gasification reactions by the catalytic effect of inorganic materials in sludge:



$$\Delta H = 132 \text{ kJ mol}^{-1}$$



$$\Delta H = -41.5 \text{ kJ mol}^{-1}$$



$$\Delta H = 206.1 \text{ kJ mol}^{-1}$$

By considering the composition of gas product obtained from pyrolysis of OS, it seems that reactions (1) and (2) are more favorable.

### 3.4. Composition of gaseous products

The composition of gas products obtained from the fixed-bed reactor is presented in Table 4. The major gaseous products were CO, hydrogen and methane for the OS, whereas CO,  $CO_2$  and  $C_3$  in the case of MS. The fact that MS produced the greater amount of  $CO_x$  may suggest that MS contains more carboxylic groups than OS. In the pyrolysis of OS, as we mentioned above, hydrogen and CO were mainly formed by the water gas reaction.

The total amount of  $H_2S$  was also determined. The amounts of  $H_2S$  were 2.00 and 1.86 wt% in the gaseous products for pyrolysis of MS and OS, respectively. It is known that most

Table 3  
Product yields from the pyrolysis of sludges (wt%)

Sludge type	MS	OS
Gas <sup>a</sup>	20.9 ± 2.3	14.9 ± 2.8
Liquid		
Aqueous	26.0 ± 1.5	14.1 ± 1.2
Oil	13.2 ± 0.9	29.8 ± 1.9
Char	39.9 ± 2.3	41.2 ± 2.8

<sup>a</sup> Calculated from mass balance.

Table 4  
Composition of the gaseous products from pyrolysis of sludge at 500 °C (expressed as mol%)

	H <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	CO	CO <sub>2</sub>
MS	4.59±0.12	3.04±0.09	1.13±0.03	11.46±1.20	5.42±0.10	1.59±0.02	–	51.34±1.52	21.43±0.91
OS	23.96±0.35	19.47±0.93	6.32±0.05	6.43±0.03	4.22±0.02	1.99±0.03	1.24±0.03	27.32±0.84	9.05±0.09

hydrogen sulphide is formed by the degradation of bacteria in sludge pyrolysis. However, in the case of oil sludge (contains no bacteria), hydrogen sulphide may mainly evolve from the degradation of organic sulphur compounds such as mercaptanes, thiophenes, etc. The other sulphur gaseous products were also determined by GC-SCD. However, the quantification of each gaseous product could not be managed since each component was in trace amount.

Moreover, pyrolysis gases from MS and OS had high gross calorific values of about 29.9 and 35.8 MJ Nm<sup>-3</sup>, respectively. Therefore, they can provide some part of the energy requirements of the pyrolysis plant. These heating values represent the mean heating values of the gas mixture, and they have been calculated from the concentration of each individual gas and its corresponding heating value. The heating values of gases are higher than those reported in the literature. This is a result of the high content of combustible gases in gas products.

The heating value is related to the gas composition and the composition of gas products depends on various parameters, such as sludge constituents, temperature, heating rate and vapor residence time. The gas product from sewage pyrolysis containing combustible gases of 19 vol% had a calorific value of 2.55 MJ Nm<sup>-3</sup> [18]. On the other hand, Menendez et al. [17] studied the microwave and conventional pyrolysis of four different sludges and found that microwave pyrolysis generated gas products with a high content (48–62%) of CO and H<sub>2</sub>, while conventional pyrolysis gave rise to a gas with an elevated proportion (ca. 25%) of hydrocarbons of high calorific value (Y8). The heating values of gases from conventional pyrolysis were 13.0–14.0 MJ Nm<sup>-3</sup>, whereas the heating values ranged from 6.6 to 8.6 MJ Nm<sup>-3</sup>.

Inguanzo et al. [14], who studied the pyrolysis of sewage sludge reported that the heating value of gases was influenced by the evolution of hydrocarbons present in the gases. A maximum heating value (25.0 MJ Nm<sup>-3</sup>) was obtained around 455 °C during pyrolysis with a heating rate of 5 °C min<sup>-1</sup>. This corresponds to the maximum release of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. At a heating rate of 60 °C min<sup>-1</sup>, the release of these gases took place over a broader temperature interval (> 600 °C) and CH<sub>4</sub>, H<sub>2</sub> and CO were higher at higher concentrations. In the case of 60 °C min<sup>-1</sup>, the maximum heating value (20.0 MJ Nm<sup>-3</sup>) was obtained at 600 °C.

### 3.5. Pyrolysis liquids

Pyrolysis liquids consisted of aqueous and oil fractions. Aqueous fractions contained mainly of water and small amounts of water soluble organics such as alcohols, ethers, aldehydes and carboxylic acids. The amount of water soluble organics in the aqueous fractions was determined by ether

extraction and found to be maximum 2 wt%. For this reason, the analysis of the aqueous fraction was outside the scope of this study.

Table 5 shows the chemical and physical properties of oils from pyrolysis of sludges. For the purpose of comparison, the chemical and physical properties of commercial diesel are also presented in Table 5. Pyrolytic oils from pyrolysis of MS and OS were denoted as PO-1 and PO-2, respectively. The amounts of hydrogen and oxygen in PO-2 were very low compared to PO-1 and oils from sludges reported in the literature [14,19,20]. Because of the high carbon content, the calorific value of PO-2 is similar to conventional liquid fuels and higher than those found by other authors from pyrolysis of sewage sludges and biomass [19,21,22]. On the other hand, the calorific value and elemental composition of oil [13], which was obtained by pyrolysis of oil sludge from a crude oil tank, was similar to that of PO-2.

The viscosity of PO-2 is slightly higher than that of diesel, whereas the viscosity of PO-1 lies in the viscosity range of fuel oil. Consequently, the low sulphur content and the high calorific value of pyrolysis oils reflect the potential of these oils for use as fuels besides being used as chemical feedstocks. A knowledge of oil composition is necessary for their utilization either as a raw material or fuel.

Pyrolytic oils are complex mixtures consisting of organic compounds from wide variety of chemical groups. To characterize the pyrolytic oil, the oils were separated into four fractions; asphaltenes, aliphatics, aromatics and polars. The compositions of pyrolytic oils are given in Table 6.

PO-2 had more aliphatic character, whereas PO-1 was rich in polars. The dominance of the polars in PO-1 is possibly due to the presence of proteins and lipids in the sludge. It was found that

Table 5  
Some properties of oils obtained from conventional pyrolysis

Pyrolytic oil type	PO-1	PO-2	Commercial diesel
Viscosity at 40 °C, cSt	30.11	5.38	2.0–4.5
GCV <sup>a</sup> , kJ/kg	32.86	43.86	45.1
Elemental composition, wt% ± standard deviation			
C <sup>b</sup>	70.9	84.5	86.5
H <sup>c</sup>	10.3	12.4	13.2
N <sup>c</sup>	7.5	0.7	<0.1
S <sup>d</sup>	0.2	0.6	<0.7
O <sup>e</sup>	11.1	1.8	
H/C	1.74	1.76	1.83

<sup>a</sup> Gross calorific value.

<sup>b</sup> Standard deviation: ±1.9.

<sup>c</sup> Standard deviation: ±0.2

<sup>d</sup> Standard deviation: ±0.1

<sup>e</sup> Standard deviation: ±1.9.

Table 6  
Composition of pyrolytic oils from sludge pyrolysis (wt%)

Sludge type	MS	OS
Asphaltene	16.0	–
Aliphatic	15.9	63.1
Aromatic	23.0	28.4
Polar	41.1	4.7

the lipid fraction (18 wt%) of a typical raw sludge was found to contain 65% straight chain carboxylic acids, 28% unsaponifiables and 7% triglycerides [23]. Boocock et al. [24] concluded that long chain carboxylic acids did survive the pyrolysis and resulted in an increase in viscosity of the oil. Generally, pyrolysis of sludge yielded liquid products which contained significant amounts of oxygenated compounds and unacceptable amounts of nitrogen and possibly sulphur. On the other hand, Shen [21] reported that the sewage sludge had a higher proportion of oxygenated aromatics and these oxygenated aromatics form the oil during low temperature pyrolysis. Although, low aromatic and polar content is desired in fuels, they are of great importance from an industrial point of view. They can be used as a source of chemicals.

Another important compounds from the point of view of the

application of the oil as a fuel is aliphatics. Ideally, the components in oil should be straight chain hydrocarbons, as these have a high heating value and lower viscosity. By considering the results from Tables 5 and 6, it is clearly seen that the oils having higher aliphatic contents have a low viscosity and a high heating value.

The aliphatic fractions were analyzed by GC/MS. The aliphatic fractions consist of *n*-alkanes, alkenes and branched hydrocarbons. Figs. 6 and 7 present typical GC/MS chromatography profiles of the aliphatics. In order to determine the distribution of these hydrocarbons in aliphatics, a semi-quantitative study was made by means of the percentage of area of the chromatographic peaks. The aliphatics of oils contained a smaller amount of *n*-alkanes, 9.14 and 6.02% for PO-1 and PO-2, respectively. However, the total amount of *n*-alkanes were 61.8 and 63.2% for PO-1 and PO-2, respectively. The majority of the linear chain hydrocarbons were distributed in the range C<sub>12</sub>–C<sub>28</sub>. However, it must be noted that some part of light hydrocarbons may have escaped by the evaporation of solvent during the fractionation of oils.

The aliphatic fractions of oils obtained from pyrolysis of sludges were also analyzed for the different boiling points by GC, according to the standard test method for boiling range

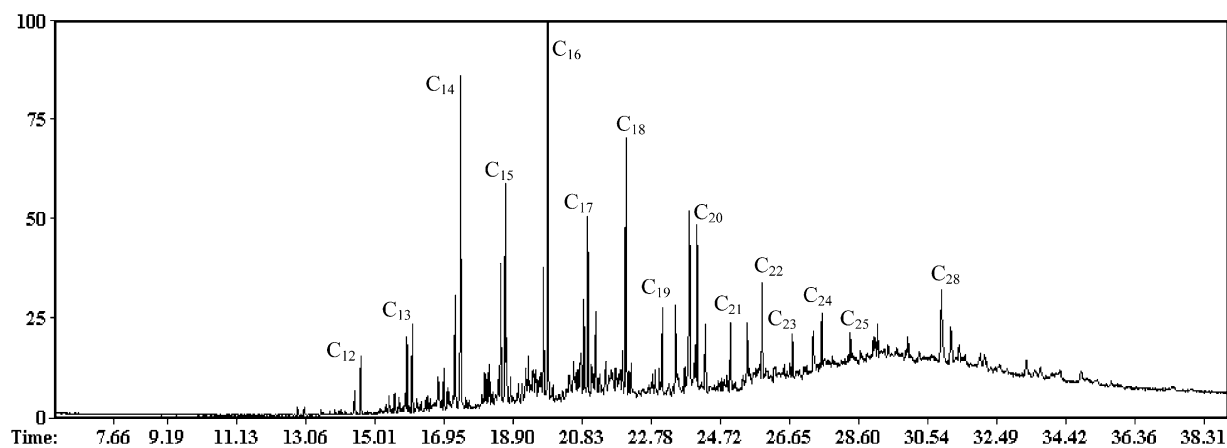


Fig. 6. GC/MS chromatogram of the aliphatic fraction in PO-1.

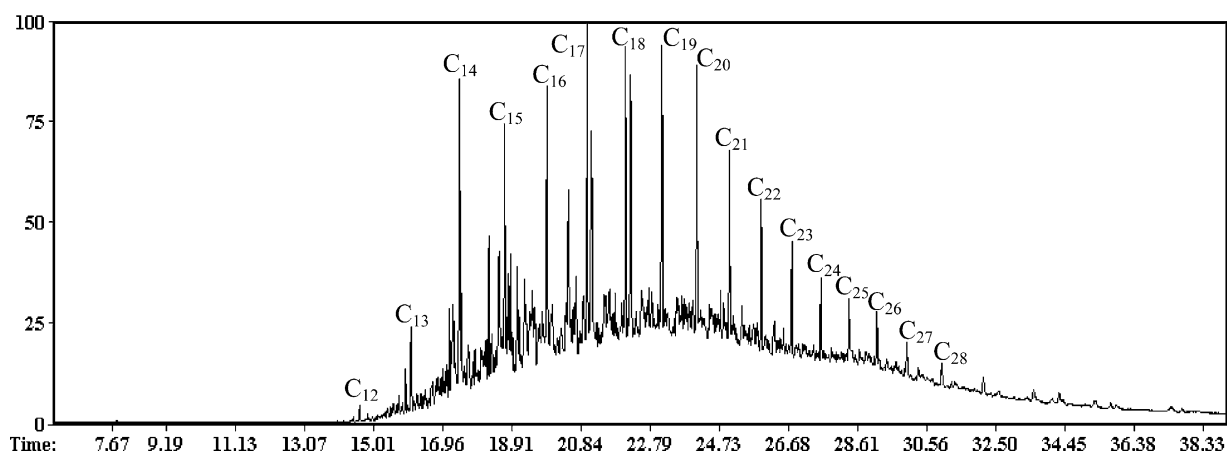


Fig. 7. GC/MS chromatogram of the aliphatic fraction in PO-2.



Table 7  
Distillation characteristic of aliphatic fractions of in pyrolytic oils and commercial fuels

	Heavy naphtha, 93–204 °C	Light gas oil, 204–343 °C	Heavy gas oil, 343–538 °C
PO-1	0	47	53
PO-2	0	70	30
Diesel	16	74	10
Fuel oil	4	46	50
Heavy oil	0	24	75

distribution of petroleum fractions (ASTM D2887). Three portions of aliphatics are cut apart as listed in Table 7. For a comparison purpose, distillation characteristics of fuel oil, heavy oil and diesel are also presented in the same table. As seen from Table 7, aliphatics in PO-2 are slightly heavier than commercial diesel, but their boiling point range is lower than fuel oil. However, the boiling point range of aliphatics in PO-1 is similar to that of fuel oil.

The functional groups of the aromatic and polar fractions in pyrolytic oils were analyzed by infrared spectroscopy (IR) to identify the basic compositional groups. Table 8 represents the functional group compositional analysis for the aromatic fractions obtained from the IR spectra. In the aromatic fractions of PO-1 the presence of aromatic carboxylic acids or  $\alpha/\beta$  unsaturated carboxylic acids was indicated by the absorbance peak of the C=O band between 1725 and 1700  $\text{cm}^{-1}$  and the C=C or C=O stretching at 1600  $\text{cm}^{-1}$ . However, in the aromatic fractions of PO-2 the stretching band at 1600  $\text{cm}^{-1}$  showed the aromatic structure because of the absence of the absorbance peak between 1725 and 1700  $\text{cm}^{-1}$ . The peaks appearing at 1060  $\text{cm}^{-1}$  and between 930 and 890  $\text{cm}^{-1}$  may indicate the presence of six and five membered cyclic hydrocarbons.

Table 9 summarizes the position and the assignment of the various peaks observed in the infrared spectra of polar fractions of the pyrolytic oils. IR spectra of the different polar fractions were essentially the same. The bond located at the 3500–3200  $\text{cm}^{-1}$  shows the presence of polymeric O–H. The absorbance peak of the C=O band between 1725 and 1700  $\text{cm}^{-1}$  and the C=O stretching band at 1600  $\text{cm}^{-1}$  indicate the presence of aromatic carboxylic acids or  $\alpha/\beta$  unsaturated carboxylic acids. It must be noted that the presence of the C–O stretching vibrations with absorbance between 1260 and 1250  $\text{cm}^{-1}$  represent the presence of ethers in the polar fraction of PO-1.

### 3.6. Pyrolytic chars

Pyrolysis of sludges yielded a char of approximately 40%. In principle, the chars obtained from pyrolysis of sewage sludge could be either incinerated, or disposed off by landfilling or used as adsorbents. The potential use of chars in these three options depends on their characteristics. Although in this study, special attention has been given to the liquid and gaseous products of pyrolysis, some properties of chars were also determined. As would be expected, the

Table 8  
Major bands in the infrared spectra of aromatic fractions

Wave number ( $\text{cm}^{-1}$ )	Type of bond	PO-1	PO-2
3200–3000	C–H stretching (aromatic)	++	++
2980–2920	C–H stretching (aliphatic)	+++	+++
2250	C $\equiv$ N stretching	+	+-
1725–1700	C=O frequency (saturated aliphatic carboxylic acid)	+	-
1600	C=C or C=O stretching (conjugate)	++	++
1480–1465	-CH <sub>2</sub> - or CH <sub>3</sub> -C (asymmetric) scissoring	++	++
1385–1380	(CH <sub>3</sub> ) <sub>2</sub> -C C–H bending	++	-
1060	6-Membered ring (cyclic aliphatic hydrocarbon)	+	+
930–890	5-Membered ring (aliphatic)	+	+
810–730	C–H out-of-plane deformation (disubstituted benzene)	+	+
700–680	C–H out-of-plane deformation (benzene)	++	++

resultant chars from sludges had a high ash content (Table 1). The high ash content makes them unattractive for use in incineration.

The chars had a relatively low surface area. Similar surface area values have been reported in the literature. The surface areas of chars obtained from the pyrolysis of an anaerobic sludge varied between 32 and 82  $\text{m}^2 \text{g}^{-1}$ , depending on the pyrolysis

Table 9  
Major bands in the infrared spectra of polar fractions

Wave number ( $\text{cm}^{-1}$ )	Type of bond	PO-1	PO-2
3500–3200	O–H stretching (polymeric)	++	++
3200–3000	C–H stretching (aromatic)	+	+
2980–2920	C–H stretching (aliphatic)	+++	+++
2250	C $\equiv$ N stretching	+	+
1725–1700	C=O frequency (saturated aliphatic carboxylic acid)	++	++
1600	C=C or C=O stretching (conjugate)	++	++
1520–1500	C–H stretching (aryl)	+	+
1480–1465	-CH <sub>2</sub> - or CH <sub>3</sub> -C (asymmetric) scissoring	++	++
1385–1380	(CH <sub>3</sub> ) <sub>2</sub> -C C–H bending	++	+
1260–1250	C–O stretching and O–H in plane bending	+	-
1175–1165	(CH <sub>3</sub> ) <sub>2</sub> -C skeletal	+	+
1060	6-Membered ring (aliphatic)	+	+
930–890	5-Membered ring (aliphatic)	+	-
700–680	C–H out-of-plane deformation (benzene)	+	+

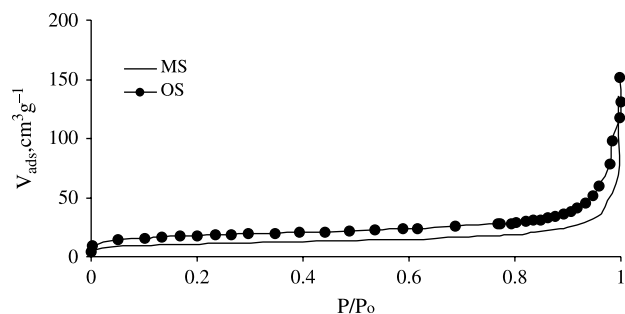


Fig. 8. Nitrogen adsorption isotherms of pyrolytic chars obtained from sludges.

conditions [25]. Lu [26] also obtained a char having a surface area of  $80 \text{ m}^2 \text{ g}^{-1}$  from an anaerobically digested sludge. Since, the total surface areas of the chars are mostly attributed to their carbon matrix, the low surface area of chars may be due to the high ash content.

On the other hand, production of sludge-based activated carbons has also been studied using different chemical agents, with the resulting solids having a surface area of  $100\text{--}400 \text{ m}^2 \text{ g}^{-1}$  [27–32]. These activated carbons were found to be usable as an adsorbent for odour control and liquid phase adsorption [28,33–35].

As seen from Fig. 8, nitrogen adsorption isotherms of pyrolytic chars correspond to isotherms of type II, indicating a less microporous structure. The chars have also low adsorptive capacity, considering the low amount of nitrogen adsorption.

As conclusion, landfilling is seen to be the main alternative for disposal of the pyrolytic chars obtained in this study.

#### 4. Conclusion

Pyrolysis of two types of sludges (mixed sludge and oil sludge) was investigated using a thermal gravimetric analyzer coupled to a quadropole mass spectrometer (TG/MS) and a fixed bed reactor.

In TG/MS experiments, two degradation steps were observed for both sludges. The first degradation step, relating to the degradation of organic structures was observed in the temperature range of  $200\text{--}500$  and  $100\text{--}350$  °C for MS and OS, respectively. In the second step ( $500\text{--}900$  °C), decomposition of inorganic materials mainly took place. The total weight losses was found to be 66 and 62 wt% for MS and OS, respectively.

In pyrolysis of sludges in the fixed-bed reactor, both the type of organic and inorganic matter in the sludges affected the product distribution of pyrolysis. Although, OS contained a greater amount of ash than MS, the char yields were similar for both OS and MS. In the case of OS pyrolysis, gasification reactions by the catalytic effect of inorganic materials in the sludge led to an increase in production of hydrogen and a decrease in the yield of the water fraction. The gas products from pyrolysis contained a high amount of combustible gases. Pyrolysis of OS produced an oil having a high calorific value with a viscosity being slightly higher than that of diesel. On the

other hand, the viscosity of the oil obtained from MS was in the range of fuel oil, but its calorific value was low.

The chemical composition of oils varied with the type of sludge. Oil from OS had more aliphatic compounds whereas oil from MS was rich in polar compounds. The resultant chars from sludges had a relatively low surface area and high ash content. Taking into account the above results, it has been concluded that the oil from OS can be used as fuel whereas the oil from MS can be considered as a feedstock. However, landfilling is the best alternative to dispose of the chars.

Consequently, for sludges used in this study, pyrolysis looks a promising solution from an environmental and economic viewpoint.

#### Acknowledgements

This work was supported by Ege University, Faculty of Science, under the contract number 2001/Fen/033. We thank DAAD (German Academic Exchange Service) for financial support and for offering us the opportunity to perform a part of this work in Institut für Chemische Technik, Universität Karlsruhe.

#### References

- [1] European Commission DG Environment-B/2. Disposal and recycling routes for sewage sludge scientific and technical sub-component report; 23/10/2001.
- [2] Bockhorn, Hornung A, Hornung U. *J Anal Appl Pyrol* 1999;50:77–101.
- [3] Yanik J, Yuksel M, Saglam M, Olukcu N, Bartle K, Frere B. *Fuel* 1995; 74(1):46–50.
- [4] Dumpelmann R, Richarz W, Stambach MR. *Can J Chem Eng* 1991;69: 953–63.
- [5] Urban DL, Antal MJ. *Fuel* 1982;61:799–806.
- [6] Ahuja P, Singh PC, Upadhyay SN, Kumar S. *Indian J Chem Technol* 1996;3:306–12.
- [7] Shie J-L, Chang C-Y, Lin J-P, Wu C-H, Lee D-J. *J Chem Technol Biotechnol* 2000;75:443–50.
- [8] Chang C-Y, Shie J-L, Lin J-P, Wu C-H, Lee D-J, Chang C-F. *Energy Fuel* 2000;14:1176–83.
- [9] Conesa JA, Marcilla A, Moral R, Moreno-Caselles J, Perez-Espinosa A. *Thermochim Acta* 1998;313:63–73.
- [10] Jakab E, Faix O, Till F, Szekely T. *J Anal Appl Pyrol* 1995;35:167–79.
- [11] Jakab E, Faix O, Till F, Szekely T. *Holzforschung* 1991;45(5):355–64.
- [12] Conesa JA, Marcilla A, Caballero JA. *J Anal Appl* 1997;43(1):59–69.
- [13] Chang C-Y, Shie J-L, Lin J-P, Wu C-H, Lee D-J, Chang C-F. *Energy Fuel* 2000;14:1176–83.
- [14] Inguanzo M, Dominguez A, Menendez JA, Blanco CG, Pis JJ. *J Anal Appl Pyrol* 2002;63:209–22.
- [15] Stambach MR, Kraaz B, Hagenbucher R, Richarz W. *Energy Fuel* 1989; 3:255–9.
- [16] Murwanashyaka JN, Pakdel H, Roy C. *J Anal Appl Pyrol* 2001;60: 219–31.
- [17] Menendez JA, Dominguea A, Inguanzo M, Pis JJ. *J Anal Appl Pyrol* 2004;71:657–67.
- [18] Midilli A, Dogru M, Howarth CG, Ling MJ, Ayhan T. *Energy Convers Manage* 2001;42:157–72.
- [19] Dominguez A, Menendez JA, Inguanzo M, Bernad JJ, Pis JJ. *J Chromatogr A* 2003;1012:193–206.
- [20] Beckers W, Schuller D, Vaizert O. *J Anal Appl Pyrol* 1999;50:17–30.
- [21] Shen L, Zhang D. *Fuel* 2005;84:809–15.

- [22] Horne PA, Williams PT. Fuel 1996;75(9):1051–9.
- [23] Boocock DGB, Konar SK, Leung A, Ly LD. Fuel 1992;71:1283–9.
- [24] Konar SK, Boocock DGB, Mao V, Liu J. Fuel 1994;73:642–6.
- [25] Bahadur NP, Boocock DGB, Konar SK. Energy Fuel 1995;9:248–56.
- [26] Lu GOM. Environ Technol 1995;16:495–9.
- [27] Font R, Fullana A, Conesa JA, Llavador F. J Anal Appl Pyrol 2001;58/59: 927–41.
- [28] Martin MJ, Artola A, Balaguer MD, Rigola M. Chem Eng J 2003;94: 231–9.
- [29] Chiang PC, You JH, Can. Can J Chem Eng 1987;65:922–7.
- [30] Lu GO. Environ Prog 1996;15:12–18.
- [31] Bagrev A, Bashkova S, Locke DC, Bandosz TJ. Environ Sci Technol 2001;35:1537–43.
- [32] Martin MJ, Artola A, Balaguer MD, Rigola MJ. Chem Technol Biotechnol 2002;77:825–33.
- [33] Otero M, Rozada F, Calvo LF, Garcia AI, Moran A. Biochem Eng J 2003; 15:59–68.
- [34] Luo GO, Lau DD. Gas Sep Purif 1996;10:103–11.
- [35] Rozada F, Calvo LF, Garcia AI, Martin-Villacorta J, Otero M. Bioresour Technol 2003;87:221–30.