



Study of bio-oils and solids from flash pyrolysis of sewage sludges

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ABSTRACT

The aim of this study was to evaluate the production of pyrolysis oil from three types of sewage sludges. The flash pyrolysis was performed at 500 °C, the maximum oil yield was 43.1%, and the water content in bio-oils obtained from secondary sludges was relatively low – 10.3% and 17.0%. GC–MS results showed that pyrolytic bio-oils of studied sludges dominantly contained fatty acids and nitrogenous compounds with potential added value.

Obtained solids had high ash content and low calorific value which make them unattractive for use in incineration. FT–IR results showed that solids gave similar IR features as notified aluminosilicates; utilization of these solids as adsorbents could be a potential valorization.

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1. Introduction

The management of municipal wastewater treatment sludges is a difficult and expensive problem. With aerobic treatment generally 0.5–1 kg of activated sludge is produced per kilogram of biological oxygen demand (BOD₅) [1,2]. The solids typically contain 60–80% organic matter in primary sludge, 70% in activated (secondary) sludge and 40–50% in digested sludge [3]. Secondary sludge contains 32–41% proteins, 5–12% lipids and 15–30% carbohydrates; digested sludge comprises 10–21% proteins, 2–17% lipids and 15–30% carbohydrates [3,4].

The common disposal processes for sewage sludge include land filling, land application and incineration. Disposal in landfills is still the most frequently chosen alternative for sludge in Europe [5]. Disposal by landfilling requires a lot of space and the soil has to be sealed adequately to prevent the leaching of toxic compounds. Land application or the use of sewage sludge as a fertilizer can result in the accumulation of pollutants, mostly toxic metals.

Thermal treatment methods (e.g. waste combustion) have been introduced to replace the land filling option. There are however limitations. One of the major barriers is the public worry that combustion processes may release volatile toxic matter into the near environment. For example, toxic heavy metals cannot be retained during the combustion process and will thus be deposited on particulate matter nearby the incineration installation. More toxic volatile organic compounds (VOC's) can be formed and released [6].

Several technologies, such as pyrolysis, are currently under investigation as an alternative to conventional combustion processes. Pyrolysis is the thermal decomposition of organic substances under oxygen-deficient circumstances [7]. Pyrolysis at relatively low temperature presents certain advantages over the other methods [8]. The volume of the solid residue is drastically reduced; the heavy metals present in the carbonaceous matrix are relatively resistant to natural lixiviation [9], the thermal treatment gives rise to gases and even bio-oils with a high energetic value so they can be used as potential fuels. The chemical properties of the bio-oil indicate it's potential to be used as a range of specialty and commodity chemicals such as fertilizers and resins [10].

Flash or fast pyrolysis is an approach to maximize the yield of liquid product. Pyrolysis oil derived from sludge in this way results in a dark brown liquid that consists of a complex mixture of oxygenated hydrocarbons. The liquid product can be stored until required or readily transported to where it can be most effectively utilized [11]. The economic viability of pyrolysis may be improved if value-added products could be produced from the solids (e.g. adsorbents), oil (e.g. fertilizers) or gas (e.g. syn-gas) [12].

2. Materials and methods

2.1. Material

Three types of sludge were studied: (a) thickened excess activated sludge (AKP); (b) dewatered digested sludge (DIG) and (c) (OLDA) was collected as dried excessive activated sludge. AKP and DIG were dried at 105 °C and then pulverized by hand-mill and stored in airtight containers.

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2.2. Experimental apparatus and procedure

The flash pyrolysis was performed in semi-continuous lab scale reactor consisting of three parts: the vertical reactor, the injection and the recuperation system [13].

Within the vertical stainless steel reactor of 2200 ml, 700 g of white sand was used as heat transfer medium. Before use, this sand was dried at 105 °C. The sand was in constant motion during the entire process to ensure a homogeneous temperature sand bed operating system. This was realized by an Archimedical screw which is perforated systematically on its whole length. The reactor was heated by a tailored heating jacket. The gas flow in the reactor was 140 ml/min of N₂ (2 × 70 ml/min) to guarantee an “oxygen-deficient” environment. The nitrogen gas entered the reactor via two ways: firstly, via the hollow shaft of the Archimedical screw in the reactor, and secondly via the injection system for the bio-mass. As the sludge injection system was started, the nitrogen flow was stopped. There was an overpressure obtained due to the pyrolysis gases, resulting in an automatically flowing of the pyrolysis products to the condensation vessel.

The injection system was manufactured in stainless steel as well. It consisted of a container with a volume of 600 ml and an injector. The sludge was injected into the reactor fed from the container via an Archimedical screw with a controlled feeding rate (25 Hz). In this way 200 g of dried sewage sludge was completely transferred to the reactor within 90 s. The recuperation system (condensation vessel (OV)), was a stainless steel collector vessel with a volume of 580 ml and was kept at room temperature. In-between the reactor and the collector, a small water cooler was constructed to quench the gases. At the output of the collector vessel, a cold trap made out of copper (kept at –196 °C with liquid nitrogen) was installed to collect the rest of condensable gases (cold finger – CF). The non-condensable gases escaped the recuperation system via the chimney.

2.3. Analysis

1. Thermogravimetric analysis (TGA) was used for analysing the sludges and solids with respect to their thermal behaviour. About 25 mg of sample was pyrolysed under approximately 35 ml/min He flow at a heating rate of 20 °C/min from room temperature (RT) to 700 °C. For the determination of fixed carbon and ash content, the gas flow was switched to oxygen with further heating to 900 °C under the same heating rate of 20 °C/min.
2. Ultimate analysis was used to determine the CHNS- and O-content.
3. Calorific value determination was performed to determine the Highest Heating Value (HHV) of the sludges, bio-oils and chars. Net calorific values in terms of DIN norm 51900-3 [14] were also calculated.
4. GC-MS analysis – the bio-oils were dissolved in methanol and analyzed by GC/MS. The GC/MS instrument was a quadrupole mass spectrometer with He as the carrier gas and a capillary column (30 m DB-WAX × 0.25 mm i.d.; 0.25 μm film thickness).
5. FT-IR spectroscopy – the bio-oil was applied as a cast film between two KBr windows. FT-IR spectra of the chars were obtained after mixing with KBr (KBr pellet).

3. Results and discussion

3.1. Feed materials characteristics

3.1.1. Thermogravimetric analysis

Thermogravimetric analysis was used for determining the residual moisture and to define the operating temperature for ther-

mal degradation of sludge in the flash-pyrolysis reactor. The weight loss up to 200 °C (1.5, 3.7 and 5.3 wt% for sludges AKP, DIG and OLDA, respectively (see Table 1)) is due to the release of free and physically bounded water. Most of the combustible matter is degraded between 200 and 500 °C. DTG-curves result for all sludges under study in one dominant peak with T_{max} at about 320 °C and a $T_{shoulder}$ at about 450 °C.

The DTG profile for AKP reveals a stepwise degradation up to 600 °C with minor losses of water. Mass loss for DIG sludge starts almost immediately and occurs over a broad temperature range with an extra mass release at enhanced temperature (600 °C–700 °C) which reflects the presence of high molecular weight compounds. The evolution of the DTG profile is less pronounced.

For OLDA, the release of water is more resolved from the thermal degradation process.

All three sludges can also be differentiated with respect to their fixed carbon formation: 20% (AKP), 8% (DIG), 18% (OLDA).

The ash content of AKP sludge and OLDA sludge is 25.0% and 27.3% respectively. The higher amount of ash content in DIG sludge was caused by anaerobic digestion, where part of the organic matter was converted to bio-gas.

Since TGA is dynamic experiment and pyrolysis is static experiment, it is decided to select 500 °C as pyrolysis working temperature.

3.1.2. Ultimate analysis

The results of ultimate analysis of studied sludges are summarized in Table 1. Amounts of carbon and nitrogen in the DIG sludge are lower compared to the two other sludges because compounds with these elements are released during anaerobic digestion (carbon in bio-gas as CH₄ and CO₂ and nitrogen in sludge liquor as N_{ammon}). A relatively high amount of sulphur in OLDA sludge is caused by the characteristics of the treated (co-treatment of urban waste waters).

The total amount of C, H, N, S and O from the ultimate analysis fits well with the amount of mass losses from thermogravimetric analysis. The high H/C ratio value indicates a high content of aliphatic hydrocarbon compounds in these sludges, while the relatively low amounts of oxygen is an indication for a minor fraction of polar compounds present in sludges. Because of the high N/C ratio, these sludges could be of great interest in view of further valorisation of the obtained bio-oil for products with added value.

Table 1
Characteristics of the sewage sludge.

	AKP	DIG	OLDA
<i>TGA analysis (wt%)^a</i>			
Moisture	1.5	3.7	5.3
Volatile matter	53.8	40.5	49.0
Fixed carbon	19.7	8.3	18.4
Ash	25.0	47.5	27.3
<i>Ultimate analysis (wt%)^a</i>			
Carbon	39.9	27.6	38.8
Hydrogen	5.9	4.4	5.6
Nitrogen	7.9	3.5	6.0
Oxygen	23.5	19.4	23.4
Sulphur	0.7	1.0	3.0
H/C molar ration	1.8	1.9	1.7
O/C molar ration	0.44	0.53	0.45
N/C molar ration	0.17	0.11	0.13
<i>Calorific value (MJ/kg)^a</i>			
Calorimetric analysis	17.1	8.8	15.4
Net calorific value	16.5	8.6	15.0

^a As prepared (dried at 105 °C, ground).

3.1.3. Calorific value determination

The calorific values of the dried sludges are in line with mass loss values from thermogravimetric analysis and ultimate analysis. Lower amounts of mass losses relate to lower calorific value. The lowest HHV and net calorific value can be assigned to the DIG sludge (8.8 MJ/kg, 8.6 MJ/kg), which has the lowest amounts of combustible matter (48.8%) and the highest ash content. AKP and OLDA sludge have similar HHV's (17.1, 15.4 MJ/kg) and net calorific values (16.5 and 15.0 MJ/kg) which is in line with their similar volatile matter content. The calorific values observed for AKP and OLDA sludge are in line with other conventional and non-conventional fuels such as low rank coal, paper and wood [15].

3.2. Pyrolysis products – general features

In each experiment, char and pyrolytic oil (bio-oil) fraction yields are determined as dry ash free mass and the gas fraction yield is calculated by mass balance. The presented values correspond with the average value of two pyrolysis experiments.

The pyrolysis product yields obtained from 3 types of sewage sludge are shown in Table 2. Some pyrolysis liquids consist of an aqueous and an oil fraction. In case of DIG sludge both, oil and

Table 2
Pyrolysis products.

Yield (wt%)	AKP sludge ^a	DIG sludge ^a	OLDA sludge ^a
<i>Bio-oil (wt%)</i>			
Vessel [oil]	29.4 ± 1.5	9.4 ± 2.0	24.4 ± 2.2
Vessel [aq.phase]	–	9.4 ± 0.5	–
Cold finger [oil]	2.7 ± 0.4	–	1.3 ± 1.3
Cold finger [aq. phase]	11.0 ± 0.5	2.9 ± 2.3	2.8 ± 2.8
Mix solids + oil	–	5.0 ± 0.3	–
Bio-oils in total	43.1 ± 0.7	26.7 ± 1.0	28.5 ± 1.9
Solids (wt%)	35.6 ± 0.5	56.0 ± 0.1	42.6 ± 1.1
Gas (wt%)	21.3 ± 1.2	17.3 ± 1.1	28.9 ± 2.9
<i>Bio-oil (wt%, daf basis)^b</i>			
Vessel [oil]	39.3 ± 2.0	18 ± 3.9	33.6 ± 3.0
Vessel [aq.phase]	–	17.8 ± 0.9	–
Cold finger [oil]	3.6 ± 0.5	–	1.8 ± 1.8
Cold finger [aq. phase]	14.7 ± 0.6	5.5 ± 0.6	3.8 ± 3.8
Mix solids + oil	–	9.6 ± 0.5	–
Bio-oils in total	57.5 ± 0.9	50.9 ± 1.9	39.2 ± 2.5
Solids (wt%, daf basis) ^b	14.1 ± 0.7	16.2 ± 0.2	21.0 ± 1.5
Gas (wt%, daf basis) ^b	28.4 ± 1.6	32.9 ± 2.1	39.8 ± 4.1
Water content in vase (v/v%)	10.3 ± 1.7	78.7 ± 0.3	17.0 ± 1.0

^a The values correspond with the average value of two pyrolysis experiments.

^b The term 'daf' represents dry ash free basis.

aqueous fractions, are observed as two separated layers in the condensation vessel. For AKP and OLDA sludge, an oil and an aqueous phase is found only in the cold finger condensate. Important is that these two phases are well separable, in contrary with pyrolysis liquids obtained from other biomass materials. Oil and aqueous fractions are separated and analyzed as such.

Additionally one more product was obtained during pyrolysis of DIG sludge: a mixture of oil and solids (collected in the connection pipe connecting reactor and condensation vessel). This mixture has a high calorific value and is classified as one of "bio-oils" products.

The amount of water in the bio-oils was determined by azeotropic distillation. The water content for bio-oil obtained by pyrolysis of AKP sludge is 10.3%, for OLDA sludge 17.0%. These values are significantly lower than the water content of bio-oils obtained from pyrolysis of other biomasses which ranges between 20 and 40% [11,13].

3.2.1. Calorific value determination

Highest heating values (HHV) as well as net calorific values of pyrolysis products are reported in Table 3. HHV of the produced oils range from 23.9 to 29.0 MJ/kg-oil, net calorific values range from 23.2 to 28.1 MJ/kg-oil and are invert proportional with the water content of bio-oils: the highest HHV is obtained for the oil fraction from DIG sludge, where the aqueous phase was removed by simple separation, because of a two phase bio-oil production.

HHV's of the chars are 5.2 (DIG), 9.9 (AKP) and 10.6 (OLDA) MJ/kg-total solids (TS). Net calorific values of the chars are 5.0, 9.6 and 10.1 MJ/kg-TS for respectively DIG, AKP and OLDA sludge.

The calorific values of the oils and chars are somewhat lower than reported by Kim [12] (36–39 MJ/kg-oil and 10–21 MJ/kg-TS). The reason for this difference is caused by the used sludge with lower HHV's.

The energy loss values shown in Table 3 are determined from an energy balance that considered the dried sludges and the pyrolysis products (oils and char) as shown by

$$E_{\text{loss}} = M_{\text{ds}}\text{HHV}_{\text{ds}} - (M_{\text{oil}}\text{HHV}_{\text{oil}} + M_{\text{char}}\text{HHV}_{\text{char}}) \quad (1)$$

where M and HHV refer to the mass and highest heating values, and the subscript ds refer to the dried sludge. It is assumed that the energy loss values (E_{loss}) are related to the energy associated with the gas phase [12]. No experimental data is available for the energy of vented gases at this moment. " E_{loss} " can be recuperated for sustaining a continuous pyrolysis system at its working temperature and if needed, used for other purposes, like drying the biomass or production of syngas (see Table 3).

Table 3
Calorific values of the sludges and the pyrolysis products.

Sample		AKP sludge		DIGESTED sludge		OLDA sludge	
		HHV/NET (MJ/kg)	Energy [E * M] (MJ)	HHV/NET (MJ/kg)	Energy [E * M] (MJ)	HHV/NET (MJ/kg)	Energy [E * M] (MJ)
Sludge	Input	17.1	3.415	8.8	1.767	15.4	3.084
		16.5		8.6		15.0	
Bio-oil	Vessel [oil]	24.7	1.455	27.9	0.527	23.9	1.167
		24.2		27.6		23.2	
	Cold finger [aq. + oil phase]	15.7	0.429	*		*	
		14.7					
	Cold finger [only oil phase]	29.0	0.157	*		*	
Mix solids + oil	28.1		20.7	0.209			
Pyrolytic solids	Pyrolytic solids	9.9	0.703	5.2	0.584	10.6	0.902
		9.6		5.0		10.1	
Gas	"Energy loss" (Eq. (1))	15.7	1.039	13.0	0.737	17.5	1.152

*Not determined because of too small amounts of samples.

Table 4
Ultimate analysis of produced bio-oils.

Ultimate analysis ^a (wt%)	AKP		DIG		OLDA	
	AKP OV	AKP CF oil	DIG OV[aq.]	DIG CF oil	OLDA OV	OLDA CF oil
Carbon	65.5	68.4	69.0	73.4	54.1	58.8
Hydrogen	8.9	8.7	9.4	9.5	8.1	8.8
Nitrogen	11.1	9.8	6.1	8.0	9.6	8.3
Oxygen	13.9	10.3	14.3	6.7	25.9	20.7
Sulphur	0.7	2.7	1.2	2.4	2.4	3.4
H/C ratio	1.63	1.53	1.64	1.56	1.79	1.79
O/C ratio	0.16	0.11	0.16	0.07	0.36	0.26
N/C ratio	0.14	0.12	0.08	0.09	0.15	0.12

^a Results normalized to 100%.

3.3. Bio-oils

3.3.1. Ultimate analysis

The results of ultimate analysis of produced bio-oils are shown in Table 4. Because of losses of volatiles during sample loading, a normalization factor is included.

Percentages of elements converted to bio-oil vs. biomass are calculated (Table 5).

The H/C ratio of bio-oil comparing to H/C ratio of sludge slightly decreases in cases of AKP and DIG sludge. This indicates higher concentration of unsaturated and aromatic compounds in bio-oils than in sludges.

H/C ratio of bio-oils produced from OLDA sludge reaches the highest values which reflect the highest amount of aliphatic carbon chains in these bio-oils.

The rather low amounts of oxygen in bio-oil can be interpreted as low concentration of polar functionalities in these bio-oils.

3.3.2. FT-IR spectroscopy and GC-MS analyses

Bio-oils from pyrolysis of sewage sludge are also studied by FT-IR and GC-MS analysis. Since only OV fraction of bio-oils obtained

by pyrolysis of AKP and OLDA sludge have significant yield, only these IR spectra are reported (Fig. 1a and b). Both OV and CF phases of bio-oil obtained from AKP and OLDA sludge are analyzed by GC-MS (Fig. 2a–d).

Pyrolytic oils are complex mixtures consisting of organic compounds with wide variety of chemical functionalities. The groups of organic compounds in bio-oils identified by GC-MS are reported in Table 6. The identified compounds can be grouped into the following classes: oxygenated hydrocarbons such as carboxylic acids and alcohols; nitrogenous compounds such as amides, amines and nitriles; compounds containing sulphur such as sulphides and sulphoxides; and hydrocarbons. Also steroids such as cholestene, cholestadiene and cholestanol are present.

Each group can be also classified into aliphatic, cyclic and aromatic compounds (also given in Table 6). Sulphur compounds are only detected as aliphatic species.

Generally, pyrolysis of these sludges yields bio-oils which contain significant amounts of oxygenated and nitrogenous compounds.

It can be seen, that IR patterns of produced bio-oils are similar, revealing that their corresponding functional groups distribution

Table 5
Elemental fraction from sludge incorporated in bio-oil, pyrolytic solid and gas.

Elements incorporated in bio-oils (%)									
	AKP OV	AKP CF oil	Total AKP	DIG OV [aq.]	DIG CF	Total DIG	OLDA OV	OLDA CF oil	Total OLDA
Carbon	48.2	4.6	52.8	47.1	7.7	54.8	34	6.1	40.1
Hydrogen	44.4	4.0	48.4	40.2	6.3	46.5	35.1	6.3	41.4
Nitrogen	41.2	3.3	44.5	32.8	6.6	39.4	39.1	5.6	44.7
Oxygen	17.3	1.2	18.5	13.9	1.0	14.9	27	3.6	30.7
Sulphur	29.4	10.4	39.8	22.6	7.0	29.6	19.5	9.2	28.4
Elements incorporated in pyrolytic solids (%)									
	AKP			DIG			OLDA		
Carbon	24.5			33.6			32.1		
Hydrogen	12.1			9.6			13.7		
Nitrogen	19.8			28.9			29.1		
Oxygen	24.8			17.9			26.2		
Sulphur	55.9			23.2			45.4		
Elements incorporated in gas (%)									
	AKP			DIG			OLDA		
Carbon	22.7			11.6			27.8		
Hydrogen	39.5			43.9			44.9		
Nitrogen	35.7			31.7			26.2		
Oxygen	56.7			67.2			43.1		
Sulphur	4.3			47.2			26.2		

Elemental fraction from sludge incorporated in bio-oil calculated with formula: $(X_{oil}/X_{ds}) * (m_{oil}/m_{ds}) * 100$ where $X = \text{wt\% of C/H/N/O}$ and $m = \text{mass}$; subscript ds refers to the dried sludge and oil to bio-oil; the value $(m_{oil}/m_{ds}) * 100$ correspond with the yield in Table 2.

e.g. carbon AKP sludge incorporated in AKP OV bio-oil: $(65.5/39.9\%) * 29.4\% = 48.2\%$.

Elemental fraction from sludge incorporated in pyrolytic solids calculated with formula: $(X_{ps}/X_{ds}) * (m_{ps}/m_{ds}) * 100$ where $X = \text{wt\% of C/H/N/O}$ and $m = \text{mass}$; subscript ds refers to the dried sludge and ps to pyrolytic solids; the value $(m_{ps}/m_{ds}) * 100$ correspond with the yield in Table 2.

e.g. carbon AKP sludge incorporated in AKP pyrolytic solids: $(27.5/39.9\%) * 35.6\% = 24.5\%$.

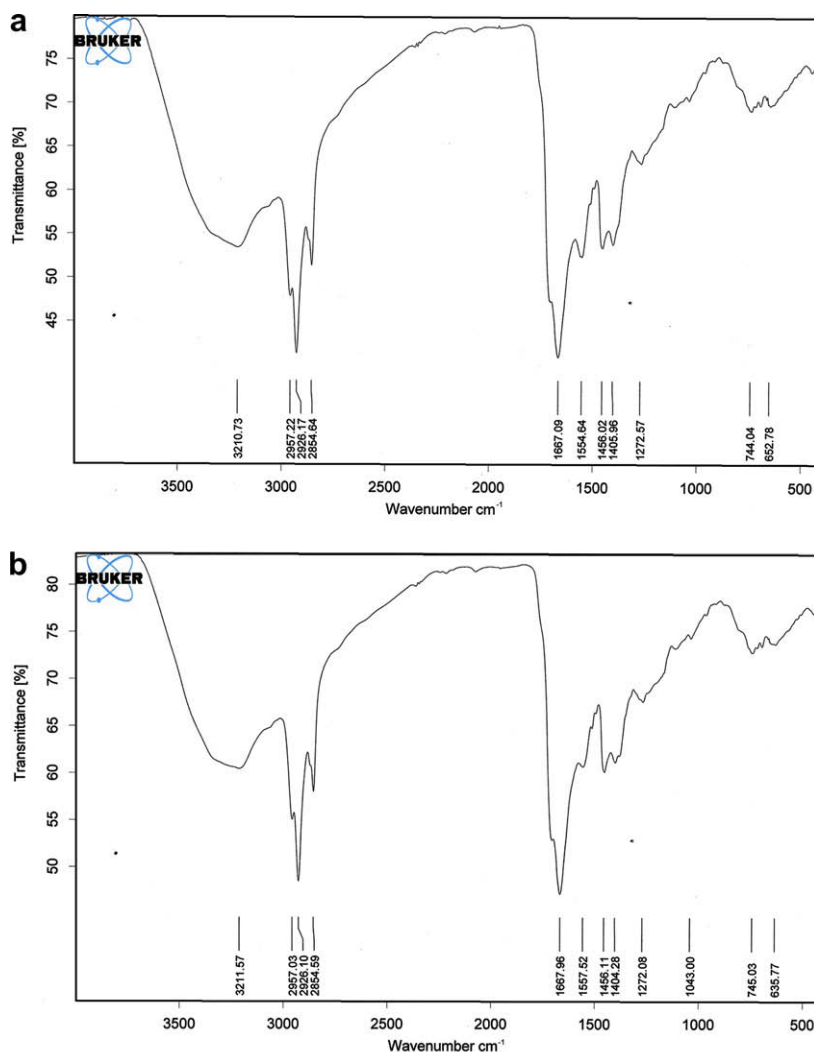


Fig. 1. FT-IR spectra of produced bio-oils from (a) OV fraction of AKP sludge and (b) OV fraction of OLDA sludge.

are similar. The presence of a large intense band of intermolecular hydrogen bonds of O–H stretching vibration at 3400 cm^{-1} can be assigned to carboxylic group and hydroxyl functionalities. The presence of carboxylic acids is further confirmed by the absorption band around 1700 cm^{-1} (typical stretching vibration from carboxylic acids). This band is more intense in case of bio-oils from OLDA sludge, reflecting the higher concentration of carboxylic acids. Absorption due to C–O vibrations are also found between 1300 and 900 cm^{-1} . GC–MS analysis shows that bio-oils from AKP sludge contain carboxylic acids (36 to 39%), bio-oils produced from OLDA sludge contain 76% carboxylic acid in case of OV phase and 64% in case of CF phase. Most of these carboxylic acids are long straight chain fatty acids (retention time-RT 19.32–25.32 min). This is in good agreement with literature. Karayildirim [16] reported that raw sludge produced oil with 65% of straight chain carboxylic acids.

Boocock [17] reported that long chain carboxylic acids survived the pyrolysis and resulted in an increase in viscosity of the oil. Bio-oil of OLDA sludge shows higher viscosity than the oil produced from AKP sludge which again is in good agreement with prior studies [17].

Other oxygenated compounds detected by GC–MS in bio-oil are mostly phenolics (RT 14.86–16.33 min). FT-IR spectra features predict the presence of amides and amines by superposition of an absorption band around 3200 cm^{-1} (N–H stretching). The pres-

ence of secondary amides is further confirmed from the absorption band at $1570\text{--}1530\text{ cm}^{-1}$. The spectral window $1500\text{--}1680\text{ cm}^{-1}$ could be assigned to phenols and amides. Specific absorption bands within this spectral window are more dominant in case of bio-oil from AKP sludge, which is confirmed by GC–MS results.

Presence of nitrogenous compounds ranges from 27% to 29% in bio-oils produced from AKP sludge and from 11% to 12% in bio-oils produced from OLDA sludge. The main nitrogenous compounds observed in the pyrolysate of studied sludges are secondary amides. Bio-oils obtained by pyrolysis of AKP sludge consist of 21% (OV phase) and 10% (CF phase) amides. Presence of amides in bio-oils from OLDA sludge amounts to 7%. Amines are present by 5% in OV phase and 12% in CF phase in bio-oils obtained by pyrolysis of AKP sludge. Bio-oils from OLDA consist of 2.5% and 3% of amines in OV and CF phase respectively.

FT-IR spectra give also an indication for the presence of nitriles ($\text{C}\equiv\text{N}$) in the spectral region $2260\text{--}2210\text{ cm}^{-1}$, which is further confirmed by GC–MS. Higher concentration of nitriles appears in CF phase (4.1% and 2.8% in pyrolytic bio-oils from AKP and OLDA sludge, respectively). These nitriles are formed by dehydration reactions of peptide bonds present in the protein fraction of the sludge.

Additional compounds detected by GC–MS are sulphur compounds, especially identified in CF phase, which is in line with re-

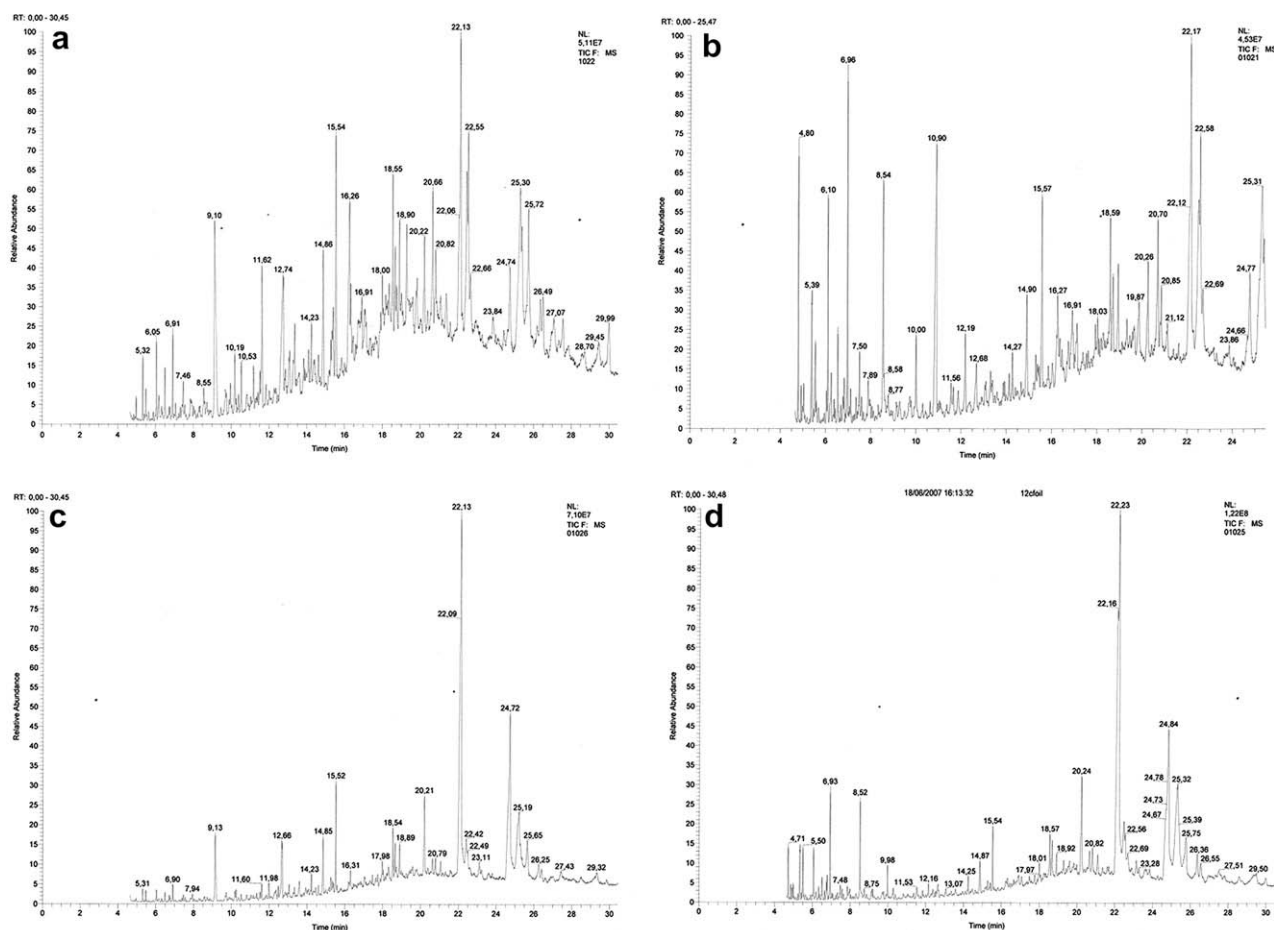


Fig. 2. GC–MS chromatograms of (a) OV phase of bio-oil from pyrolysis of AKP sludge; (b) CF-oil phase of bio-oil from pyrolysis of AKP sludge; (c) OV phase of bio-oil from pyrolysis of OLDA sludge and (d) CF-oil phase of bio-oil from pyrolysis of OLDA sludge.

Table 6

GC–MS analysis of the produced bio-oils from AKP and OLDA sludge.

GC–MS analysis (wt%) ^a	AKP – OV	AKP – CF oil	OLDA – OV	OLDA – CF oil
Classified by composition				
<i>Oxygenated compounds</i>				
Fatty acids	39	36	76	64
Alcohols	8.9	7.1	8.0	3.8
Others	2.5	1.6	0.0	0.4
Total oxygen compounds	51	44	84	68
<i>Nitrogenated compounds</i>				
Amides	21	10	7	7
Amines	5	12	2.5	3.0
Nitriles	2.8	4.1	1.9	2.8
Total nitrogenated compounds	29	26	11	13
<i>Sulphur compounds</i>				
	1.3	8.7	0	5.7
<i>Hydrocarbones</i>				
	4.1	10.9	0.8	6.3
<i>Steroids</i>				
	6.9	2.6	3.4	3.7
<i>Not identified</i>				
	8.3	6.9	1.0	4.2
Classified by structure				
Aliphatic	52	52	79	77
Cyclic	21	20	7	9
Aromatic	19	21	14	10
Not identified	8	7	1	4

^a Results normalized to 100%.

sults of ultimate analysis. Minor amounts are detected in OV phase (<1.5%).

Long aliphatic carbon chains are verified within the IR spectral window 3000–2800 cm⁻¹, dedicated to C–H stretching vibrations,

as well as the deformation bands between 1470 and 1430 cm⁻¹, and rocking CH₂ vibrations stretching at 722 cm⁻¹. Most of these aliphatic carbon chains are structural moieties of fatty acids. Presence of pure hydrocarbons is limited (0.8–10.9%).

Table 7
Characteristics of solids.

TGA analysis (wt%)	AKP	DIG	OLDA
Ash	57.9	75.1	58.1
Ultimate analysis of chars (wt%)			
Carbon	27.5	15.6	29.2
Hydrogen	2.0	1.4	1.8
Nitrogen	4.4	1.7	4.1
Oxygen	16.4	14.6	14.4
Sulphur	1.1	1.5	3.2
H/C molar ratio	0.87	1.08	0.74
O/C molar ratio	0.45	0.70	0.37
N/C molar ratio	0.14	0.09	0.12

The absorption bands in the spectral region 3100–3000 cm^{-1} (sp^2 C–H stretching vibration) can be related to the aromaticity and unsaturation of the bio-oil. Minor concentration of aromatics (ethylbenzene and styrene) are identified by GC–MS especially in CF-oil phases.

Last group detected by GC–MS are steroids (RT 26.42–30.0). Their presence in bio-oils produced from sludge was also reported by Dominguez [6,18].

3.4. Solids

The solids obtained from pyrolysis of sewage sludge could be, either incinerated for energy recuperation, disposed off by landfilling or used as adsorbents [16]. The potential use of solids in these three options depends on their chemical characteristics. Some properties of pyrolytic solids are therefore determined, such as ash content (TGA), the calorific value, CHNS-O element analysis and FT–IR features.

3.4.1. Thermogravimetric and ultimate analysis

The high ash content (see Table 7) together with low calorific value (Table 3) make chars unattractive for use in incineration. Results of ultimate analysis also show that chars have relatively very high amounts of sulphur. Percentage of elements which are incorporated in the pyrolytic solids is calculated by comparing results of ultimate analysis of input material. Most of the organic components are converted to pyrolysis bio-oils or gases, (for example pyrolytic solids contains 12.1%, 9.6% and 13.7% of hydrogen for AKP, DIG and OLDA, respectively).

3.4.2. FT–IR analysis

The IR spectra reveal the presence of the characteristics patterns of alumina-silicates (stretching vibration at 3500–3300 cm^{-1} , 1650–1600 cm^{-1} , 550–450 cm^{-1} and 1100–1000 cm^{-1}).

Spectra of the char from pyrolysis of OLDA and DIG sludge show also the specific absorption bands at 1430 for carbonates. The diagnostic IR bands at 875 and at 715 cm^{-1} can be assigned to CaCO_3 . (Confirmation – overtones at 2500 cm^{-1} and 1800 cm^{-1}).

4. Conclusions

Our study confirms that sewage sludge is suitable feed material for production of bio-oil by flash pyrolysis. Yields of bio-oils based on ash free biomass range from 39.2% to 57.5%. The best results, concerning to pyrolysis products, are obtained with AKP sludge: 57.5% of organic matter is converted to bio-oil with calorific value of 24.7 MJ/kg and also the water content was the lowest: 10.3%.

FT–IR and GC–MS analysis demonstrate that bio-oil is a complex mixture with a variety of components. However, both analyses prove that the fraction of aromatic compounds is low. GC–MS

analyses confirm that fatty acids are the most dominant group. In the application of the oil as a fuel, it is preferred that the compounds in the oil are straight chain hydrocarbons as they have a high heating value [19]. Low aromatic and polar content is also desirable for energy valorization.

Utilization of bio-oil produced from pyrolysis of sewage sludge as feed material seems also possible. High distribution of fatty acid can lead to extraction of these acids and their utilization in chemical industry. High presence of nitrogenous compounds can improve added value of bio-oils by isolation of these compounds from the bio-oil. Esterification is also another option.

FT–IR analysis of chars shows that chars have similar IR features as notified aluminosilicates. Aluminosilicates are used as adsorbents; utilization of pyrolytic solids as adsorbents should be further studied for potential added value of chars. The high ash content and low calorimetric value make them unattractive for use in incineration.

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