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# Influence of the Pyrolysis Temperature on Sewage Sludge Product Distribution, Bio-Oil, and Char Properties

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## S Supporting Information

**ABSTRACT:** Fast pyrolysis may be used for sewage sludge treatment with the advantages of a significant reduction of solid waste volume and production of a bio-oil that can be used as fuel. A study of the influence of the reaction temperature on sewage sludge pyrolysis has been carried out using a pyrolysis centrifugal reactor (PCR) at 475, 525, 575, and 625 °C. Maxima of both organic oil yield of 41 wt % on a dry ash free feedstock basis (daf) and a sludge oil energy recovery of 50% were obtained at 575 °C. The water-insoluble fraction, molecular-weight distribution, higher heating value (HHV), and thermal behaviors of sludge oils were found to be considerably influenced by the applied pyrolysis temperatures. The sludge oil properties obtained at the optimal temperature of 575 °C were a HHV of 25.5 MJ/kg, a water-insoluble fraction of 18.7 wt %, a viscosity of 43.6 mPa s at 40 °C, a mean molecular weight of 392 g/mol, and metal concentrations lower than 0.14 wt % on a dry basis (db). Less optimal oil properties with respect to industrial applications were observed for oil samples obtained at 475 and 625 °C. Char properties of the 575 °C sample were an ash content of 81 wt % and a HHV of 6.1 MJ/kg db. A total of 95% of the sewage sludge phosphorus content was recovered in the char. The solid waste amount (char compared to sludge) was reduced to 52% on a bulk volume basis at the pyrolysis temperature of 575 °C.

## INTRODUCTION

Sewage sludge produced from a wastewater treatment plant consists of a mixture of undigested organics (plant residue, paper, oils, food, and fecal material), microorganisms, and inorganic material. Traditionally, the most common ways to manage sewage sludge disposal are landfilling and agricultural reuse. However, some heavy metals are toxic to plants and may also be transferred to humans through their presence in crops. Therefore, the legislation of the European Union (EU, Directive 86/278/CEE)<sup>1</sup> was issued to qualify sewage sludge used in agriculture, and the threshold values show in Table 1 must be fulfilled regarding the accumulation of sewage sludge

on land. Several European countries have even stricter regulations. As a result, the disposal of sewage sludge is becoming of increasing concern in the EU, where sewage sludge disposal<sup>2</sup> was estimated to be 40% for landfilling and 37% for farmland applications in 2008. However, because environmental standards may become stricter in the future, the sewage sludge proportion used on farmland will probably be reduced. Consequently, the treatment cost of sludge disposal will increase.

In European countries, annual sewage sludge production exceeds 10 million tons/year (2010).<sup>2,3</sup> Sewage sludge has volatile contents of 40–88 wt % on a dry basis (db) and higher heating values (HHVs) of 11–26 MJ/kg db.<sup>2</sup> Thus, the sewage sludge is a potential important feedstock for thermal conversions, such as gasification, fast pyrolysis, and incineration processes that can reduce the sewage sludge volume and use the sludge energy content. In recent years, the treatment of sewage sludge by fast pyrolysis has been demonstrated to be a promising alternative to farmland and landfilling applications.<sup>4–9</sup> Fast pyrolysis using a high heating rate has been considered as a process not only for treating sewage sludge that can considerably reduce the volume of solid waste but also can produce a bio-oil, which can be used as fuel for boilers and also may be upgraded to a transport fuel. Many pyrolysis reactor types, such as bubbling and circulating fluidized-bed reactors, ablative reactors, auger reactors, and rotating cone reactors,

**Table 1. Limit Values for the Amount of Heavy Metals That May Be Added Annually to Agricultural Land Based on a 10 Year Average (kg ha<sup>-1</sup> year<sup>-1</sup>)<sup>1</sup>**

parameters	limit values (kg ha <sup>-1</sup> year <sup>-1</sup> ) <sup>a</sup>
cadmium	0.15
copper	12
nickel	3
lead	15
zinc	30
mercury	0.1
chromium <sup>b</sup>	

<sup>a</sup>The threshold values were issued in 1986. <sup>b</sup>It is not possible at this stage to fix limit values for chromium. The EU council will fix these values on the basis of proposals to be submitted by the commission within 1 year following notification of this directive.

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have been developed to obtain a high oil yield.<sup>10,11</sup> The fast pyrolysis reactors typically achieve heating rates of 700–1500 K/s.<sup>12,13</sup> The pyrolysis centrifuge reactor, developed in the CHEC center at the DTU Chemical Engineering, uses a high centrifugal force to gain a high feedstock heating rate.<sup>12</sup> The main advantages of this concept compared to fluid-bed reactors are a compact design that uses a low flow rate of carrier gas. The effects of the applied operational conditions of sewage sludge fast pyrolysis have been studied by several authors.<sup>5,9–11</sup> It is pointed out that the applied pyrolysis temperature is a main parameter that directly influences the properties of the pyrolysis products and the product distributions. The temperature influences the pyrolysis reactions, secondary cracking reactions, char formation, and polymerization reactions.

Similar to wood and straw pyrolysis oils, sewage sludge pyrolysis oil has a high viscosity and relatively low stability (phase separation)<sup>10,14,15</sup> when compared to a heating oil no. 2; this may lead to limited industrial applications. Besides, sewage sludge oil is known to have a lower oxygen content, HHV, and higher nitrogen and sulfur contents compared to the wood and straw oils.<sup>8,9,15,16</sup> Although, the sludge oil has high nitrogen and sulfur contents that cause an increase of NO<sub>x</sub> and SO<sub>x</sub> emissions if the sludge oil is combusted in boilers, the sludge oil has gained attention because of a high heating value (27–33 MJ/kg db)<sup>8,9,15,16</sup> and the fact that the oil is produced from a waste material. Upgrading of the sludge oil by a hydrotreating process is a possible next step to reduce the nitrogen and sulfur contents and also increase the heating value of the sludge oil, which thereby could be used as a feedstock for conventional refineries.

Some studies investigated the influence of the sewage sludge fast pyrolysis temperature on product yields (gas, bio-oil, and char)<sup>5,9–11</sup> and chemical components that have been analyzed by gas chromatography–mass spectrometry (GC–MS).<sup>17,18</sup> The sludge oil is comprised of components soluble in water or solvents, derivatives of sewage sludge constituents that are partially pyrolyzed during fast pyrolysis, and oligomers/polymers formed by condensation of vapors.<sup>19,20</sup> A complete chemical analysis of sewage sludge bio-oil is difficult to obtain. Only a fraction of about 32–44% of lignocellulosic oil<sup>21</sup> (and probably a similar proportion for sewage sludge oil) can be detected by GC.

Little is presently known about the influence of the pyrolysis temperature on properties of the sludge oils, which are important with respect to industrial applications. The objectives of this work were to study the effect of the pyrolysis temperature in the range of 475–625 °C on the product distributions (gas, reaction water, organic oil, and char yields) as well as bio-oil properties (HHV, water-insoluble fraction, molecular mass distribution, ash content, viscosity, density, thermal behavior, and elemental distributions) and char properties (ash content, HHV, particle-size distributions, and morphology) of sewage sludge pyrolyzed at a high heating rate.

## EXPERIMENTAL SECTION

**Experimental Apparatus.** The pyrolysis centrifuge reactor (PCR) shown in Figure 1 is described in detail elsewhere.<sup>22</sup> The centrifugal reactor is made of stainless steel and has an inner diameter of 85 mm. It is electrically heated by four independent heating zones along the reactor length. The pyrolysis of sludge takes place inside the reactor, whereby char, bio-oil, and gas are produced. Large char particles are removed by a change-in-flow separator, whereas fine char particles are collected by a cyclone. The change-in-flow separator and cyclone were heated to 420 °C to avoid tar condensation and blocking of the tubes.

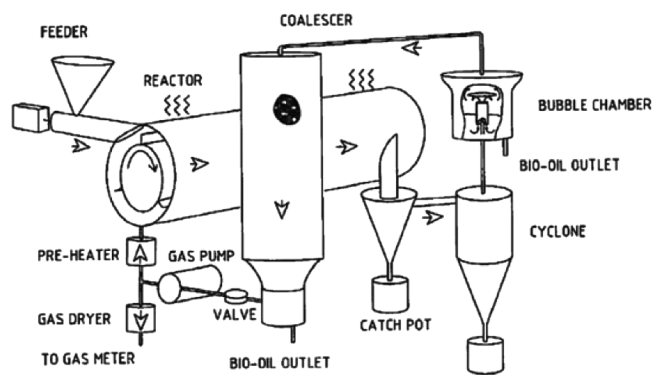


Figure 1. Sketch of the PCR.

The vapor products are condensed in a bubble chamber filled with isopropanol as a condensing solvent. The temperature in the bubble chamber is controlled to be 30–40 °C by means of a cooling water system. Possible ester formation reactions between isopropanol and carboxylic acids are believed to be negligible at the low temperature and in the absence of strong acid or base catalysts. The isopropanol was also used as a condensing solvent in fast pyrolysis experiments by Fonts et al.<sup>8,9</sup> The light oil fraction and aerosols are further condensed by a coalescer filled with Rockwool. A recycled gas flow maintains a desired gas residence time in the reactor. The gas is pumped back to a preheater and heated to around 400 °C before being fed back to the reactor. The gas products are dried by a water condenser and a gas filter to remove liquid before coming to a gas meter.

The liquid fraction collected from the bubble chamber, coalescer, and water condenser is filtered through a Whatman filter paper (pore size of 20–25 μm). The char left on the filter is washed thoroughly by ethanol and acetone and then dried under an infrared light bulb within 10 min. The char yield is determined from the chars collected in the char separator, the cyclone, and the char left on the filter paper. The bio-oil yield is determined from the liquid that passed through the filter paper. The gas volume was measured using a gas flow meter. An average molecular mass of sewage sludge pyrolysis gas produced at reactor temperatures of 475–600 °C was found to be from 26 to 32 g/mol.<sup>7,9</sup> The average molecular mass of the gas in the present study was assumed to be 29 g/mol, and this value was used to calculate the gas mass yield in this study. Thus, the inaccuracy of the gas yield relative to the feedstock is probably ±1.5 wt % on a dry ash free feedstock basis (daf).

In this study, the PCR was operated with constant operation conditions: a rotor speed of 14800 rpm, a gas reactor residence time of 0.8 s, a feeding rate of 1.3 kg/h, a total experimental time of 20 min, and a feed consumption of around 430 g sludge for each run. Before a pyrolysis experiment, the sewage sludge was purged with nitrogen to remove air and the sludge was then introduced into the reactor by the screw feeder.

With respect to practical implications, it was observed that, during the sewage sludge PCR pyrolysis experiments conducted at a low temperature (475 °C), a blockage of the nozzle connecting the cyclone and the bubble chamber appeared when experiments were performed for longer times than 20 min. The phenomenon does not appear when using wood or straw feedstocks for the PCR pyrolysis experiments. This indicates that the sewage sludge oils produced at the low temperature may contain some sludge derivatives and fine char particles, which probably agglomerate to form solid particles because of insufficient heat transfer at the low temperature of the nozzle. The deposit of these particles probably caused the blockage.

### Characterization of the Sewage Sludge and Sludge Char.

Proximate, ultimate, and element analyses were carried out on the sewage sludge feedstock, which had a particle size of 45–830 μm. The sludge char samples were analyzed by the following methods: the moisture content by ASTM D2216, the ash content by ASTM D1102-84, the particle size by sieve analysis with sieve sizes of 45–1000 μm, HHV by a bomb calorimeter (IKA C-200), total CHN by a flash

combustion (Thermo Finnigan, Flash EA1112), Cl and S by inductively coupled plasma–optical emission spectroscopy (ICP–OES) axial, and Al, Ca, Fe, K, Mg, Na, P, Ti, Si, Cr, Zn, and Cd by ICP–OES radial. The oxygen content was calculated by difference.

The raw non-digested sewage sludge was collected from a Danish wastewater treatment plant in the town of Store Heddinge. The sludge was dried before pyrolyzing in the PCR. The results of proximate, ultimate, and element analyses of the feedstock sewage sludge are presented in Table 2. The sludge contains a high ash content of 47 wt

**Table 2. Characteristics of Sewage Sludge**

proximate analysis	
moisture (wt %)	7.3
volatile matter (wt %) (determined at 950 °C)	38.0
fixed carbon (wt %)	7.9
ash (wt %) (determined at 550 °C)	46.8
ultimate analysis	
C (wt % db) <sup>a</sup>	28.0
H (wt % db)	3.4
O (wt % db) <sup>b</sup>	10.3
S (wt % db)	0.9
N (wt % db)	4.0
HHV (MJ/kg db)	10.9
element analysis	
Cl (wt % db)	0.05
P (wt % db)	3.41
Al (wt % db)	1.77
Fe (wt % db)	8.07
Si (wt % db)	8.25
Ti (wt % db)	0.23
Ca (wt % db)	3.71
K (wt % db)	0.67
Mg (wt % db)	0.43
Na (wt % db)	0.26
Cd (mg/kg db)	0.84
Cr (mg/kg db)	69.8
Zn (mg/kg db)	1035

<sup>a</sup>db = dry feed basis. <sup>b</sup>O% = 100% – ash% – C% – H% – N% – S%.

% (as received). The total alkali and earth alkali metal content (Ca, K, Na, and Mg) was found to be 5.03 wt % db. These alkali metals are known to act as catalysts for the pyrolysis reactions<sup>23–25</sup> and have a large effect on the pyrolysis yield and product compositions.<sup>23</sup> Fahmi et al.<sup>23</sup> showed that the organic oil yield increased 11 wt % when *Festuca arundinacea* was washed to reduce the content of alkali and earth alkali metals (Na, K, Ca, and Mg) from 3.56 to 0.84 wt % db.

Thermogravimetric analysis (TGA) of sewage sludge was carried out at a temperature range of 110–1000 °C and at a constant heating rate of 10 °C/min in a N<sub>2</sub> flow using a TGA instrument (Netzsch STA 449 F1).

The morphologies and dominant element distributions of chars were investigated by means of a scanning electron microscope (SEM, INSPECT) equipped with an energy-dispersive X-ray (EDX) detector.

**Characterization of the Bio-Oil Product.** To obtain bio-oil samples without solvents, the isopropanol solvent was removed from the bio-oils by a rotary vacuum evaporator at a temperature of 37 °C. This method was also used to remove isopropanol solvent by Fonts et al.<sup>8,9</sup> About 15–22 wt % of water and small amounts of light organic species (less than 3 wt %) of the bio-oil samples were lost during the solvent removal (for further information, see the Supporting Information). The loss of some light organic species may have a minor influence on the viscosity of the sludge oil samples.

The properties of the bio-oil were measured by the following methods: the water content by a Karl Fischer titration (Metrohm-701KT titrino), the ash content by ASTM D1102-84, the HHV by a

bomb calorimeter (IKA C-200), the viscosity by a rotational viscometer (PAAR AMV 200), the density by a density meter (Anton paar, DMA 4100), the total CHN content by a flash combustion (Thermo Finnigan, Flash EA1112), Cl and S by ICP–OES axial, and Al, Ca, Fe, K, Mg, Na, P, Ti, Si, Cr, Zn, and Cd by ICP–OES radial.

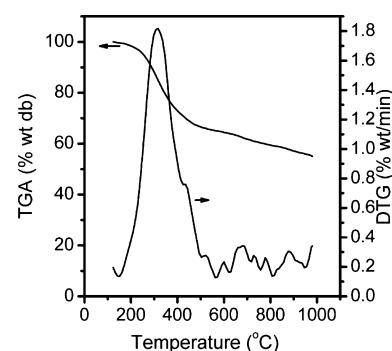
The molecular-weight distribution was analyzed by size-exclusion chromatography (SEC) using the following instrument: Viscotek GPCmax VE-2001 equipped with Viscotek TriSEC model 302 triple detector using two PLgel mixed-D columns from Polymer Laboratories. The samples were run in tetrahydrofuran (THF) at 30 °C (1 mL min<sup>−1</sup>). The molar-mass characteristics were calculated using polystyrene standards (162–371 000 g/mol). To take a representative sample for SEC analysis, the bio-oils were diluted with ethanol to make it homogeneous and then passed through a 0.2 μm filter.

The water-insoluble fraction of the oil samples were measured according to Ba et al.<sup>19</sup> A total of 5 g of bio-oil was slowly dropped into 500 mL of chilled water under strong stirring for 2 h to precipitate all components of the water-insoluble fraction. The mixture was filtered and then washed in deionized water under strong stirring for 14 h. Subsequently, the mixture was filtered by filter paper with a pore size of 0.2 μm. The filtered sample was dried at vacuum at a temperature of 60 °C.

Thermal behaviors of the bio-oils were analyzed by the TGA (STA, Netzsch STA 449 F1). A total of 8–10 mg samples were heated from room temperature to 1000 °C at a constant heating rate of 10 °C/min under N<sub>2</sub> flow.

## RESULTS AND DISCUSSION

**Product Distributions of the Sewage Sludge PCR Pyrolysis.** TGA has been used to characterize sewage sludge.<sup>18,26,28</sup> TGA and differential thermogravimetry (DTG) pyrolysis analysis results of the feedstock sewage sludge with a heating rate of 10 °C/min are shown in Figure 2. The major



**Figure 2.** TGA and DTG for pyrolysis of the dried sewage sludge. The sludge sample was heated at 10 °C/min to 1000 °C in nitrogen.

mass loss of the sewage sludge takes place in a temperature range of 150–575 °C. The peak mass loss at temperatures of 155–400 and 400–575 °C are probably the decomposition of less complex organic structures (probably mainly cellulose from paper, cardboard, wood garden waste, and kitchen waste) and decomposition of more complex organic structures, respectively. The TGA char yields at 400 and 575 °C are 72 and 65 wt % db and correspond to char fractions of 53 and 16 wt % daf, respectively. These results imply that the sewage sludge probably has a higher proportion of simple organic structures than that of complex organic structures. The sewage sludge contains high amounts of volatile inorganic elements, such as S (0.9 wt % db), Na (0.26 wt % db), K (0.67 wt % db), and Cl (0.05 wt % db) (see Table 2). Thus, the small peaks observed



at temperatures higher than 575 °C seen on the DTG curve may be caused by the release of some inorganic compounds.<sup>27,28</sup>

The sewage sludge PCR pyrolysis experiments were performed at four different temperatures of 475, 525, 575, and 625 °C. The temperature range is believed to cover the full decomposition temperatures of sewage sludge.<sup>18,26,28</sup> The experiments were performed twice at each pyrolysis temperature to ensure reproducible pyrolysis product determinations. The obtained mass balance closures were in a range of 92–99%. The average product yields of two experiments and standard deviations ( $\pm 2$ ) are shown in Figure 3. The char yield

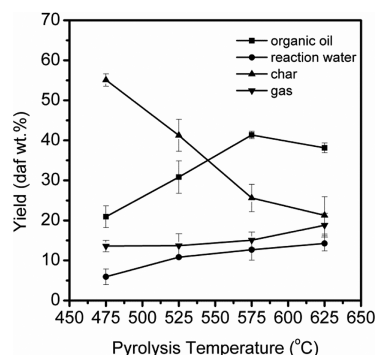


Figure 3. Pyrolytic product yields of sewage sludge (daf).

decreases from approximately 55 to less than 21 wt % daf, whereas the gas yield slightly increases from 14 to 19 wt % daf when the temperature increases from 475 to 625 °C. The increase in the organic oil yield is accompanied by a decrease in the char yield when increasing the temperature from 475 to 575 °C. The organic oil yield reaches a maximum of 41 wt % daf (bio-oil yield of 54 wt % daf) at 575 °C. An increase of the gas yield together with a slight decrease of the organic oil yield (38 wt % daf) is obtained at 625 °C. This is probably caused by secondary reactions of bio-oil decomposition. Thus, the optimal temperature to obtain a maximal organic oil yield is found to be around 575 °C in this study. The trends of the product yields and the optimal temperature found in this work are consistent with other pyrolysis sewage sludge studies, where the sewage sludge samples obtained a maximum bio-oil yield of 31–52 wt % daf at 525–575 °C in fluidized-bed reactors.<sup>5,9</sup> The PCR char yield of 25 wt % daf obtained at the reactor temperature of 575 °C, and this is 6 wt % daf lower than the TGA char yield (31 wt % daf or 65 wt % db) (see Figure 2) obtained at 575 °C. Different evolution trends of reaction water yield are found in the literature.<sup>6,29</sup> An increased trend of the reaction water yield from 2 to 20 wt % daf was observed by Piskorz et al.<sup>6</sup> when the reaction temperature was increased from 350 to 700 °C, while a decreased trend of the reaction water yield from 16 to 13 wt % db with an increasing temperature from 400 to 550 °C was obtained by Shen et al.<sup>29</sup> for sewage sludge pyrolysis. The different evolution trends with respect to the pyrolysis temperature are probably caused by differences of pyrolysis conditions, reactor types, and feedstock. In this study, the reaction water yields vary from 6 wt % daf at 475 °C to 14 wt % daf at a pyrolysis temperature at 625 °C, as seen in Figure 3.

The heating rate has a large influence on the pyrolysis product distributions. A modeling of the PCR process has indicated that a typical particle initial heating rate of 200–1000 K/s is obtained,<sup>12</sup> which is much higher than that of fixed-bed

reactors having a heating rate of less than 100 K/min.<sup>25,30</sup> Bio-oil yields obtained from these low heating rate reactors were 22–42 wt % daf<sup>26,31</sup> and are 1.3–1.6 times lower than that of the PCR.

The recovered energy contents in bio-oil and char were calculated by the product yields and their heating values. Figure 4 shows the energy distributions in the bio-oil and char. The

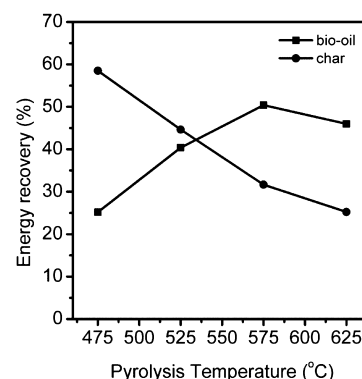


Figure 4. Energy recovered in bio-oil and char compared to the feedstock sewage sludge.

char energy recovery decreased from about 59 to 32%, whereas the oil energy recovery increased from 25 to 50% when the temperature was increased from 475 to 575 °C. Thus, most of the energy content was transferred from the char into the bio-oil. At the temperature of 625 °C, the oil energy recovery slightly decreased because of secondary reactions of the sludge oil. Thus, in this study, the maximal bio-oil energy recovery of 50% is obtained at a pyrolysis temperature of 575 °C. The optimal temperature to obtain a maximum bio-oil energy recovery is similar to the optimal temperature for obtaining a maximum organic oil yield.

**Characterization of the Bio-Oil.** Table 3 summarized some of the results from the analysis of the sewage sludge bio-oil samples. In this work, the water-insoluble fractions were 16–19 wt % of the 525 and 575 °C oil samples, which is lower than the level found in the 475 and 625 °C samples. A typical water-insoluble fraction contains oligomeric materials, polycyclic aromatic hydrocarbons (PAHs), and extractives and has a mean molecular weight in a broad range of 650–6900 g/mol (for lignin-cellulosic bio-oil).<sup>19,32</sup> It probably causes instability of the bio-oil (phase separation and viscosity increase during storage). The HHV on a dry basis of sludge oils obtained at the pyrolysis temperature of 525–575 °C is 1.7 times higher than that of the 475 °C sludge oil. The trend of HHV evolution in this work is consistent with those reported by Park et al.,<sup>18</sup> who also investigated sewage sludge pyrolysis. The fraction of cellulose derivatives containing a high oxygen content probably decreases with an increasing pyrolysis temperature, leading to a decreased oxygen content of sludge oils produced at a higher pyrolysis temperature.

SEC was used to investigate the molecular-weight distribution of the bio-oil samples. As seen in Figure 5, the three oil samples obtained from pyrolysis temperatures of 525, 575, and 625 °C had two main peaks of 90–340 and 340–3500 g/mol, whereas the 475 °C sample had a broader peak of 90–3500 g/mol. When the temperature increased from 525 to 625 °C, the magnitude of the first peak decreased along with an increase of the second peak. The condensation of aromatic compounds

Table 3. Bio-Oil Properties

sludge oil sample	457 °C	525 °C	575 °C	625 °C
water content (wt %)	27.8 ± 1.8	30.3 ± 1.2	30.2 ± 0.8	28.5 ± 1.1
water-soluble content (wt %) <sup>a</sup>	41.1	54	51.1	49.5
water-insoluble fraction (wt %)	31.1	15.7	18.7	21.8
ash content (wt %)	0.8	0.2	0.4	0.2
HHV (MJ/kg db)	15.5 ± 1.1	24.8 ± 0.2	25.5 ± 0.1	23.1 ± 0.5
density (g/mL)	1.08 ± 0.02	1.04 ± 0.01	1.03 ± 0.02	1.07 ± 0.02
viscosity at 40 °C (mPa s)	81.1 ± 0.8	36.9 ± 0.6	43.6 ± 1.3	137.7 ± 3.1
mean molecular weight, $M_w$ (g/mol)	430	386	392	481

<sup>a</sup>Water-soluble fraction = 100 – water-insoluble fraction – water content.

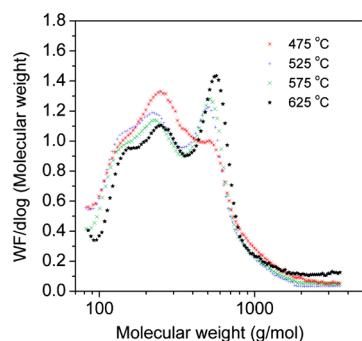


Figure 5. Size-exclusion chromatography (SEC) determined molecular-weight distribution of sludge oils.

during biomass pyrolysis was studied by Elliot.<sup>20</sup> When the pyrolysis temperature is higher than 600 °C, alkyl groups are cleaved from phenolics, resulting in cyclization reactions,<sup>20</sup> and eventually, PAHs are formed at 700 °C. The findings in this study suggest that a recombination of volatiles to form the high molecular compounds (molecular mass of 450–700 g/mol) perhaps take place in the 625 °C samples (see Figure 5), resulting in an increase of the mean molecular mass (see Table 3). The mean molecule mass ( $M_w$ ) values of the 475 and 625 °C samples were 430 and 481 g/mol, which are higher than those of the 525 and 575 °C samples. These results are consistent with the water-insoluble fractions of the oil samples (see Table 3), which are supposed to consist of condensed aromatic compounds and sewage sludge derivatives, which are supposed to have a molecular mass of 700–3500 g/mol.<sup>33</sup> This indicates that a higher content of these derivatives is observed in the 475 °C sludge oil sample and also a higher condensed aromatic content is presented in the 625 °C sludge oil sample.

Oil viscosities have been found to be related to average molecular weight.<sup>34</sup> In this work, the measured oil viscosity values are around 40 mPa s for the 525 and 575 °C samples and 81 and 137 mPa s for the 475 and 625 °C oil samples, respectively (see Table 3). A lowering of the oil viscosities from 157 to 115 cSt with an increasing pyrolysis temperature from 400 to 550 °C was also observed by Shen and Zhang,<sup>29</sup> who pyrolyzed a mixture of sewage sludge and putrescible garbage.

TGA can be used to characterize the evaporation, thermal degradation, and combustion behavior of bio-oil. The TGA and DTG experimental data of the sludge oil samples made using a heating rate of 10 °C/min up to a temperature of 1000 °C in a nitrogen gas flow are shown in Figure 6. On the basis of the DTG curves, the same pattern with two main mass loss peaks at 40–200 and 200–500 °C are observed for the four sludge oil samples. The first peak (at temperatures of 40–200 °C) of the sludge oil samples is probably evaporation of water (28–30 wt

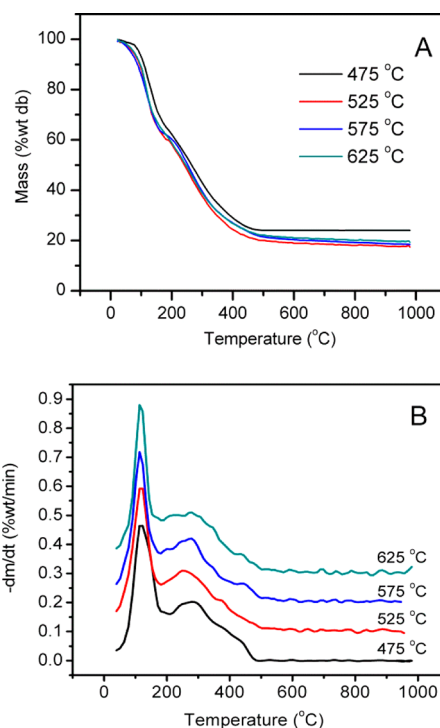


Figure 6. (A) TGA and (B) DTG of sewage sludge oil produced at 475, 525, 575, and 625 °C in a N<sub>2</sub> flow.

% content of the bio-oil samples) and light volatile components. The second peak (at temperatures of 200–500 °C) is probably the evaporation, cracking, and polymerization of high molecular fractions that could contain monolignols, moderate volatile polar compounds, mono- and polysugars, extractive-derived compounds (fatty and resin acids, paraffins, and phenanthrenes),<sup>33</sup> and sewage sludge derivatives.

On the basis of the mass loss TGA profiles (see Figure 6A), water contents determined by Karl Fischer titration, and ash contents determined by ASTM D1102-84, the bio-oil compounds are classified into three fractions: light organics, medium organics, and pyrolytic chars, as shown in Table 4. The oils produced at the different temperatures were reasonably similar; only the 475 °C oil sample deviated. The light organic fraction of the 475 °C sample (11.6 wt % daf) was lower than that of the other samples (15.5–17.6 wt % daf). It is believed that a pyrolysis temperature higher than 475 °C increases the cracking of volatiles to form more gas (see Figure 3) and also increases the light organic oil fraction. This indicates that the light organic fraction of the sludge oils of 12–18 wt % daf can be distilled. The medium organic fractions that correspond to the second peak are on a level of 52–55 wt % daf for all of the

Table 4. Bio-Oil Component Distribution

	on a wet basis				on a dry and ash-free basis			
pyrolysis temperature (°C)	457	525	575	625	457	525	575	625
water (wt %) <sup>a</sup>	27.8	30.3	30.2	28.6				
light organic fraction (wt %) <sup>b</sup>	8.4	11.5	10.8	12.6	11.6	16.5	15.5	17.6
medium organic fraction (wt %) <sup>c</sup>	39.7	38.2	37.6	36.8	55.0	54.8	53.9	51.5
pyrolytic char fraction (wt %) <sup>d</sup>	23.4	19.8	20.0	22.0	32.4	28.4	28.6	30.8
ash (wt %) <sup>e</sup>	0.8	0.2	0.4	0.2				

<sup>a</sup>Determined by Karl Fischer titration. <sup>b</sup>Determined from room temperature to 200 °C and subtraction of the water content. <sup>c</sup>Determined from the 200–500 °C section of the TGA curve. <sup>d</sup>Determined as the weight at 500 °C on the TGA curve and subtraction of the ash content. <sup>e</sup>Determined by ASTM D1102-84.

Table 5. HHV Value and Elemental Compositions of Bio-Oil from Various Materials (db)<sup>a</sup>

bio-oil	C (wt %)	H (wt %)	O (wt %)	N (wt %)	S (wt %)	HHV (MJ/kg)	bio-oil yield (wt % daf)	technology <sup>b</sup>	reference
pine sawdust	53.4	4.9	41.7	nd <sup>c</sup>	0.01	22	73	FBR	35
brown forest residue	56.5	4.4	38.2	0.41	0.04	23	66	FBR	35
green forest residue	55.3	5.2	39.0	0.40	0.03	22	59	FBR	35
eucalyptus	53.3	5.2	41.3	0.13	0.03	21	71	FBR	35
barley straw	54.2	3.3	40.7	1.84	nd	23	55	FBR	35
Timothy hay	52.9	4.1	42.0	0.99	nd	22	62	FBR	35
reed canarygrass	54.1	4.7	40.4	0.83	nd	22	76	FBR	35
pine wood	62.7	5.8	31.3	0.01	0.02	26		AR	36
oak wood	60.9	2.0	36.8	0.03	0.03	24		AR	36
pine bark	67.3	4.8	27.3	0.04	0.04	23		AR	36
oak park	58.3	3.6	37.3	0.36	0.36	24		AR	36
sewage sludge <sup>d</sup>	53.7	7.4	27.6	9.6	1.8	25	54	PCR	this work
sewage sludge	58.4	8.4	22.3	9.8	0.9	30	49	FBR	15
sewage sludge						27–33		FBR	8
sewage sludge						31–32	48–52	FBR	9
sewage sludge						23–28	39–58	FBR	16

<sup>a</sup>Calculated from available data. <sup>b</sup>AR, auger reactor; FBR, fluidized-bed reactor; and PCR, pyrolysis centrifugal reactor. <sup>c</sup>nd = not detected. <sup>d</sup>Oil produced at the pyrolysis temperature of 575 °C.

oil samples. Elliot et al.<sup>20</sup> distilled several different bio-oils by vacuum distillation, and distillation data were converted to atmospheric pressure using a petroleum hydrocarbon vapor pressure chart. The distillation residues were obtained to be of a wide range level of 47–78 wt % db at a final temperature of 390 °C. Coke formation was observed at around 205–210 °C, and bio-oil decompositions were initiated at around 280 °C. It was noted that bio-oil cannot be distilled at a temperature higher than 210 °C. Thus, the majority of the medium organic fraction when heated above 210 °C will decompose to generate pyrolytic char and lower molecular weight species. The pyrolytic char fraction of the 475 °C sample is higher than that of the other oil samples. The obtained char fractions (see Table 4) show the same tendencies as that of the water-insoluble fractions (see Table 3). Tuya et al.,<sup>19</sup> who analyzed softwood bark pyrolytic oil, showed that an oil sample with a higher water-insoluble fraction will form a higher pyrolytic char fraction when the oil is heated.

The elemental compositions, heating values, and bio-oil yields of different pyrolysis oils are shown in Table 5. Sewage sludge pyrolysis obtains a lower bio-oil yield than that of wood probably because of the high ash content (especially alkali content). However, sewage sludge has a lower oxygen content (22–28 wt % db), probably leading to a higher sewage pyrolysis oil HHV when compared to wood oils.

The analysis of the element distributions in sludge oil and char were carried out on the 575 °C samples, and the results are shown in Table 6. The contents of carbon, hydrogen, and

Table 6. Element Analyses and Element Recoveries of the 575 °C Bio-Oil and Char (db)

element	char	bio-oil	element recovery <sup>a</sup> (%)		
			char	bio-oil	total (char + bio-oil)
C (wt %)	14.6	53.7	32	38	70
H (wt %)	1.0	7.4	18	71	89
O (wt %) <sup>b</sup>	2.1	27.6	10	74	84
S (wt %)	0.5	1.8	36	39	75
N (wt %)	1.8	9.6	27	48	75
ash (wt %)	80.3	0.57	97	0.3	97
Cl (wt %)	0.04	0.12	49	48.0	97
Al (wt %)	2.68	0.006	92	0.1	92
Fe (wt %)	12.45	0.14	94	0.6	95
P (wt %)	5.29	0.01	95	0.4	95
Si (wt %)	12.85	0.02	95	1.5	96
Ti (wt %)	0.33	0.00	87	0.8	88
Ca (wt %)	5.49	0.09	90	1.8	92
K (wt %)	1.03	0.04	94	0.1	94
Mg (wt %)	0.64	0.01	91	0.0	91
Na (wt %)	0.41	0.02	96	0.0	96
Cd (mg/kg)	1.16	0.10	84	3.0	87
Cr (mg/kg)	111.5	0.51	97	0.2	98
Zn (mg/kg)	1495	97.80	88	2.3	90

<sup>a</sup>Calculated on the basis of a dry feedstock basis. <sup>b</sup>O% = 100% – ash% – C% – H% – N% – S%.

oxygen are 53.7, 7.4, and 27.6 wt % db in the bio-oil, respectively. The nitrogen and sulfur contents in the bio-oil were 9.6 and 1.8 wt %, respectively, and much higher than those of lignocellulosic oils, with typical levels of 0.03–1.8 wt % db nitrogen and 0.0–0.36 wt % db sulfur (see Table 5). The sewage sludge nitrogen and sulfur were transferred 39 and 48% to the bio-oil and 36 and 27% to the char, respectively. The recoveries of nitrogen and sulfur in the total bio-oil and char are 75%, and this indicates that some nitrogen and sulfur are probably released to the gas phase. Because the nitrogen and sulfur contents in sludge oil are so high, it may cause corrosion of equipment and environmental problems related to  $\text{NO}_x$  and  $\text{SO}_2$  emissions when the oil is combusted.

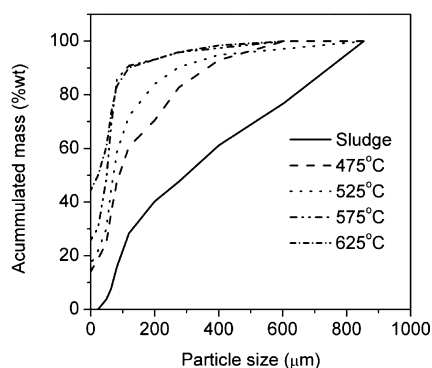
The contents of some ash-forming elements and heavy metals (Cl, Al, Fe, P, Si, Ti, Ca, K, Mg, Na, Cd, Cr, and Zn) in the char and bio-oil as well as recovered fractions are shown in Table 6. During the sludge pyrolysis at 575 °C, most of the metallic elements remain in the char (element recoveries of 84–97%); thus, the bio-oil has low levels of metals (0.0–0.14 wt %), with the most abundant elements being Fe (0.14 wt % db), Cl (0.12 wt % db), and Ca (0.09 wt % db). The lower levels of metal contents in the oils can probably be obtained if the PCR char separation system is improved. The incomplete recovery of metallic elements in the char and oil (88–98%) is believed mainly to be caused by the limited mass balance of 94% obtained for the 575 °C samples rather than metals contained in the pyrolysis gas product (with the exception being Cl and S that may also be present in the gas). The low concentration of K (0.04 wt %) and Cl (0.12 wt %) in the sludge oil should make it possible to avoid slagging, fouling, and aerosol formation problems when the oil is used for combustion or gasification.<sup>37</sup>

**Characterization of the Biochar.** Table 7 shows the ash content, organic content, and heating values of the generated

**Table 7. Sludge Char Properties**

pyrolysis temperature (°C)	457	525	575	625
ash content (wt % db)	71.3	73.8	80.5	82.3
organic content (wt % db)	28.7	26.2	19.5	17.7
HHV (MJ/kg db)	8.8	7.9	6.1	5.1

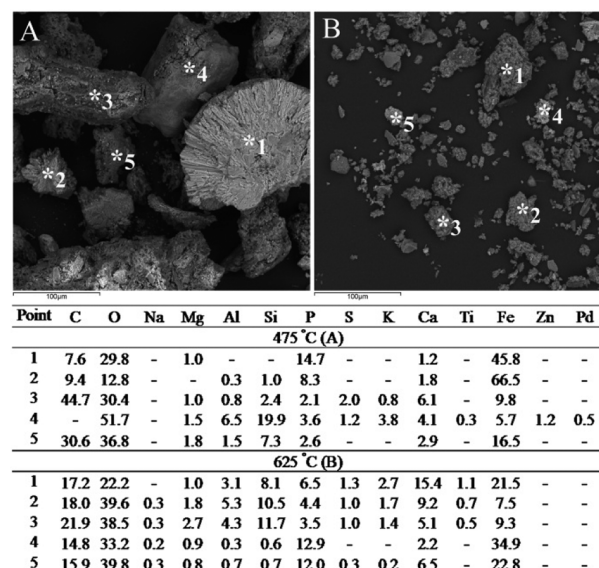
chars. The ash content of the chars rises from 71 to 82 wt % along with a decrease from 29 to 18 wt % of the organic char content when the pyrolysis temperature is increased from 475 to 625 °C. The sewage sludge and the char particle-size distributions are shown in Figure 7. The feedstock experiences



**Figure 7.** Particle-size distribution of char.

high mechanical stress in the PCR, and char exposed to higher temperatures is often more fragile. As a result, the fraction of the char particles less than 90 μm increases from 52 to 88 wt % when the pyrolysis temperature is increased from 475 to 625 °C.

When the inorganic element analysis of the 575 °C sample is taken into account (see Table 6), most metal elements in the sewage sludge are concentrated in the char product. SEM images of the 475 and 625 °C char samples are presented in Figure 8, and they confirm the results of the char particle-size



**Figure 8.** SEM-EDX of chars of sewage sludge (A at 475 °C and B at 625 °C).

distribution measurements. Obviously, the char obtained at 475 °C has a larger particle size than the 625 °C char, and both char samples exhibit diverse particle shapes. EDX was used to identify the predominant elements at some selected points. As seen in panels A and B of Figure 8, elements such as Fe, P, Al, Ca, Mg, Si, Na, and K obtain a considerable non-uniform distribution in the char particles at both low and high reaction temperatures. A similar phenomenon was reported by Ábrego et al. on sewage sludge char.<sup>38</sup>

In principle, the sludge chars may be managed by incineration or disposal on farmland or landfilling. With the high ash contents of 71–83 wt % and the low HHVs of 5.1–8.8 MJ/kg, the sludge chars are unattractive for combusting to use the energy content. However, the high contents of N, P, K, Ca, Mg, and S that are all important macronutrients of fertilizer could make the sludge char valuable as a fertilizer, especially phosphorus, which is a scarce element. With 95 wt % of phosphorus recovered in the char (see Table 6), fast pyrolysis is a promising method to recycle phosphorus into soil. The leaching of diffident phosphorus from pyrolysis char and the phosphorus nutrient availability in soil were studied by Bridle et al.<sup>39</sup> and Liu et al.<sup>40</sup> The results from these studies show that it is possible to use pyrolysis char on soil to provide phosphorus. A significant release of heavy metals with low boiling points (e.g., As, Hg, Cd, and Se) from sewage sludge was observed during carbonization above 550 °C,<sup>41</sup> whereas heavy metals with high boiling points (e.g., Pb, Co, Ni, Cu, Zn, and Sr) remained in a sludge char. Thus, if the sludge char is used on farmland, the heavy metal contents of the char (see Tables 1



and 6) limited by Directive 86/278/CEE<sup>1</sup> must be adequately taken into account. Landfilling is also a practical method to manage the sludge char disposal. In terms of sewage sludge treatment, the solid waste amount (from sludge to ash-rich char) is reduced to about 44 wt % on a mass basis and 52% on a bulk volume basis.

## CONCLUSION

The product distributions of fast sewage sludge pyrolysis with respect to organic oil, gas, char, and reaction water were determined using reactor temperatures in the range of 475–625 °C, and the char and bio-oil properties were investigated. Similar to conventional biomass pyrolysis, an increasing gas yield and a decreasing char yield were observed with an increased temperature. A maximal organic oil yield of 41 wt % daf and a maximal bio-oil energy recovery of 50% were obtained at the optimal reactor pyrolysis temperature of 575 °C.

Measurements of the molecular-weight distributions of the sludge oil indicate that the condensed aromatic content increases when the pyrolysis temperature is increased from 525 to 625 °C, while higher contents of the sewage sludge derivatives were observed in the low-temperature bio-oil of 475 °C in this study. This can partially explain the observed differences of HHV, viscosity, and thermal behaviors of the sludge oils. A sludge oil was obtained at the optimal reactor temperature of 575 °C with a HHV of 25.1 MJ/kg, a water-insoluble fraction of 18.7 wt %, a viscosity of 43.6 mPa s at 40 °C, an average molecular weight of 392 g/mol, and metallic concentrations lower than 0.14 wt %, while less optimal oil properties with respect to industrial applications were found for the 475 and 625 °C oil samples. High sulfur and nitrogen contents of the sludge oil compared to conventional bio-oil from biomass may limit the further industrial applications of the sludge oil. The char properties of the 575 °C char sample were an ash content of 81 wt % db and a HHV of 6.1 MJ/kg db, where 95 wt % of the sewage sludge phosphorus content was recovered in the char. The solid waste bulk volume (the char compared to the sludge) was reduced 52% by pyrolysis at 575 °C. It is seen that the fast pyrolysis process provides a promising method to reduce the cost for landfilling and produce a bio-oil that can be used as a fuel.

## ASSOCIATED CONTENT

### Supporting Information

Calculation of water and light fraction loss during solvent removal. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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