Distribution of ash forming elements during pyrolysis of municipal wastewater sludge and sludge from milk processing factories

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Abstract

In the long term, there is a need for alternative methods to recover energy and nutrients from increasing volumes of sludge generated from wastewater treatment plants. Pyrolysis can be an interesting option, which can reduce health and environmental risks, while providing an avenue for the recovery of energy and nutrients. One of the main concerns related to thermal conversion technologies is the release and fate of heavy metals and contaminants existing in the feedstock. Therefore, a detailed understanding of the transformation pathways of problematic compounds is necessary to assess the suitability of pyrolysis.

In this study pyrolysis of dried dairy sludge and sewage sludge was carried out using a simple laboratory fixed bed reactor. Characterisation of the feedstock and pyrolysis products was performed through proximate and ultimate analysis and the content of major and minor ash forming elements were determined. The mass balance information obtained from the experimental tests was used for an indicative distribution of Al, Ca, Fe, K, Mg, Na, P, S, Si, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Ti, V and Zn between solid and liquid pyrolysis products.

Results indicate that distribution of major elements between pyrolysis products was similar for dairy sludge and sewage sludge, with Ca, Mg, Fe, P, Si, Al, Na and K predominantly retained in pyrolysis chars (pyrogenic solids). However, substantial quantities of Al, K, Na and Si were detected in pyrolysis oil and in the aqueous fraction. The heavy metals and trace elements were mainly retained in the pyrolysis chars (pyrogenic solids) with the exception of As, Ba, Cd, Se, Sb and Pb, which were also detected in the liquid products.

Keywords

Dairy processing sludge, sewage sludge, pyrolysis, heavy metals, ash forming elements

1. Introduction

In recent years, pyrolysis has gained an increased attention as an alternative disposal method for sewage sludge [1-3]. According to a study by Samolada and Zabaniotou [1], pyrolysis can be an optimal thermochemical treatment option compared to gasification and incineration. Pyrolysis can reduce health and environmental risks from problematic wastes [4-6] while providing an avenue for the recovery of energy and nutrients [7,1]. Pyrolysis is the thermal decomposition of carbonaceous material in an inert atmosphere into gaseous, liquid and solid products. Pyrolysis gas contains the non-condensable low-molecular-mass gases such as H_2, CO, CH_4, C_2H_4, C_2H_6 and CO_2. The liquid product contains the condensable volatile compounds, water and water-soluble organics [8]. The solid residue obtained (char) is comprised mainly of carbon and ash. Pyrolysis product yields are affected by the process conditions including temperature, reactor residence time as well as feedstock properties. Slow pyrolysis is generally characterised by relative mild temperatures (350-700°C) and heating rates [1]. One of the main concerns related to thermal conversion technologies is the release of heavy metals and contaminants like NH_3, HCl, HCN, H_2S [9]. The low pyrolysis temperature is responsible for the absence of heavy metals in the pyrolysis gas, which remain concentrated mostly in the resulting carbonaceous solid product [4,10]. The potential application of all pyrolysis products greatly depends on the presence of various contaminants. According to [11] the heavy metal speciation distribution is an important indicator for evaluating pyrolysis as a disposal method and further application of the char.

Wastewater sludge is the organic by-product of municipal wastewater treatment. It consists of the solids, which are removed from wastewater during the treatment process. Treatment methods can be mechanical, biological or chemical. Organic matter in sewage sludge mainly consist of proteins, carbohydrates and lipids [19]. Sludge from wastewater treatment plants is commonly applied to agricultural land as a fertiliser [20,6]. The re-use of sludge is the most encouraged outlet, according to current EU waste policy objectives which also permit optional methods that provide the best overall environmental outcome.

The dairy industry accounts for approximately 30% of Irish agri-food exports, with 80 % of milk products being exported [12]. In order to promote growth within this sector, the Irish government has adopted strategies that offer scope for significant expansion with the aim to increase milk production by 50% overall by 2020 using the average of the outputs from 2007 to 2009 as a baseline. An increase in primary production will inevitably lead to an increase in the generation of processing waste such as sludge from the treatment of wastewater from milk processing plants. The composition of dairy sludge depends on the type of products being manufactured and cleaning process deployed at the plant. In general, there are two main sludge types: i) chemical sludge which is a mixture of fat, grease, oil and suspended solid particles removed from raw effluent in the waste water treatment plant together with some proteins and minerals by dissolved air flotation (DAF) and ii) biological sludge which is an organic material, containing suspended solids and non-biodegradable pollutants such as heavy metals resulting from biological aerobic, anaerobic or anoxic waste water treatment processes [12,13]. In Ireland the majority of sludge is land spread, e.g. in 2004 around 120,661 tonnes of dairy sludge was land spread [14]. Some sludge are sterilised and stabilised by composting and then returned to the land. DAF sludge is sometimes used as a feedstock for anaerobic digestion. However, milk fat is not easily bio-degraded and causes technological issues [15,16]. When dairy sludge are used as an organic, nutrient rich fertiliser [17] a strict code of practice must be complied with for the spreading of organic dairy sludge once a Nutrient Management Plan has been approved by the Environmental Protection Agency [18]. Drawbacks of land spreading include local oversupply due to high transport costs, which results in sludge being spread on lands in the vicinity of the dairy factories also weather conditions could constrain the land spreading. Local oversupply can lead to accumulation of certain substances in soil through annual application over many years.

Therefore, in the long term, there is a need to find alternative methods to recover energy and nutrients from sewage sludge and sludge generated from milk processing plants. This study is part of two separate projects, which investigate the potential of pyrolysis as a conversion technology for sludge from milk processing factories in the frame of state-founded Dairy Processing Technology Centre and sludge from municipal wastewater treatment plants in the frame of the state-funded OF-PYR project. In this study, samples of dairy sludge (DS) and sewage sludge (SS) were pyrolysed using a fixed bed reactor in order to measure the amount of pyrolysis products and determine their proximate properties and content of major and minor ash forming elements. A distribution of nine major and 16 minor elements between pyrolysis char and liquid products (oil and water) was investigated.

2. Materials and Methods

2.1 Sludge samples

Dairy processing sludge samples from three milk processing plants and sludge from three different municipal wastewater treatment plants (WWTP) in Ireland are the focus of this work. The range of milk products produced by the dairy companies at the time when sludge sample were collected is presented in Table 1.

Table 1. Milk products produced by dairy companies.

Milk processing company	Products						
DS-1	Butter Butter oil	Speciality powders	Whey powders (sweet)	Demineralised whey	Casein (acid, rennet)	Cheese	-
DS-2	-	Skim milk powder	Whey powders	-	-	Cheese	Base
DS-3-DAF	Butter	Skim milk powder	Whey powders (acid)	-	Casein (acid)	-	-

The dairy sludge samples were of two types: sludge after biological treatment processes with cationic polyelectrolyte addition to aid coagulation (DS-1 and DS-2) and a sample of sludge from a dissolved air floatation process (DS-3-DAF). Two of the municipal wastewater sludge samples were obtained as dried pellets (SS-1) and

granules (SS-2) while the third sample (SS-4), in a form of cake from belt press, which was bench dried before pyrolysis.

2.2 Pyrolysis

All DS and SS-4 samples were bench dried at ambient temperature and then pyrolysed in a laboratory scale fixed bed reactor. The pyrolysis set-up consisted of a quartz tube reactor (I.D./O.D. of 45/50 mm and a total length of 600 mm) coupled with a condenser cooler and a twin-neck round-bottom receiving flask where the pyrolysis liquid was collected [19]. The condenser outer jacket was cooled through circulation of a refrigerated liquid at -5°C. The outlet of the receiving flask was connected to a rubber tube fitted with a connector which enabled gas sampling or connection to an extraction hood, where the permanent gases were discharged. The quartz tube reactor was wrapped with a heating tape (Omegalux, USA) and two layers of woven high-temperature insulation were wrapped around the outside of the heating tape. An electro-thermal power regulator (Cole-Parmer, UK) was used to supply the heating tape with electricity. The heating section of the reactor was approximately 300 mm long. A batch of dried sludge in a steal-mesh basket was placed in the reactor, heated to 700°C, and kept at this temperature for 10 minutes during which the feedstock was pyrolysed. The product gas generated was cooled to room temperature while passing through the cooler, and a sample of gas was collected. Then the heating jacket was turned off and the char was cooled to room temperature while still in the reactor. The char yield was obtained as the ratio between mass of the char after pyrolysis and the initial sample mass. The vast majority of pyrolysis liquid was collected in the receiving flask; however, some of the oil/tar condensed on the cool parts of the experimental set-up. Therefore, in order to account for this fraction before and after each series of pyrolysis runs, the reactor with the heating tape and insulation, the receiving flask, the dry condenser, the rubber stopper and all of the connected glass ware were weighed and the mass of liquid fraction was obtained.

2.3 Analysis

Analysis of proximate and ultimate properties of the dried sludge samples and the pyrolysis chars were carried out by Celignis Analytical, Ireland. The proximate properties of the sludge samples were analysed according to BS EN 14774-1: 2009 (moisture content), BS EN 15403: 2011 (ash content) and BS EN 15402: 2011 (volatile matter content). The elemental composition (C, H, N, S) was determined using a Vario EL cube elemental analyser. Inorganic constituents were measured using inductively coupled plasma optical emission spectrometry (Agilent 5100 ICP-OES fitted with an SPS4 auto-sampler) after nitric acid and hydrogen peroxide and hydrofluoric acid (HNO_3-H_2O_2-HF) digestion in a microwave oven according to BS EN 15290:2011. Before digestion, sludge and char samples were ashed at 550°C. Duplicate samples of sludge and pyrolysis solids were ashed, digested and analysed. In order to measure content of inorganic components in the liquid products 1g of pyrolysis liquid was digested using HNO_3-H_2O_2-HF in a microwave oven according to BS EN 15290:2011.

2.4 Mass fraction

The mass fraction was used to illustrate the retention of major and minor elements in sludge derived solid and liquid products, and was calculated according to following equation

$$Mass\ fraction\ \% = \frac{Mi}{M_0} \qquad (1)$$

where M_i is the mass of elements in a certain product and M_0 is the mass of elements in a dry sludge when results on a dry basis are reported (Fig. 5, 6, 7 and 8) or in sludge which contained some moisture when pyrolysed (Fig. 9, 10, 11 and 12).

3. Results

3.1 Properties of municipal and dairy sludge

In Table 2 the properties of the different types of dried sludge are presented. In all tested sludge samples, relatively high volatile matter content (from 55 - 67 wt. %) and high ash content (from 23 - 36 wt. %) was observed (dry basis). This indicated that during high temperature decomposition most of the organic content of the dried sludge formed vapour-phase products (non-condensable permanent gases and condensable compounds) but also significant amounts remained in the form of solid residue. The nitrogen content was high, between 5 and 7 wt. % for SS and DS-1 and 2, it was the lowest in DS-3-DAF at 1.5 wt. %. High nitrogen content was one typical characteristics of dairy sludge as well as sewage sludge resulting from biological and chemical treatment of defatted effluent [13]. The sulphur content in most sludge samples was from 0.5 to 1 wt. % with exception of DS-3-DAF which contained only 0.1 wt. %.

Table 2. Proximate and ultimate properties of sludge types.

Properties, wt. %	DS-1	DS-2	DS-3-DAF	SS-1	SS-2	SS-4
Moisture, ar.	87.10	67.62	67.70	9.78	6.06	84.90
Moisture, after bench drying	18.55	9.51	6.24	-	-	5.67
Ash content, db.	36.28	23.66	36.41	32.13	28.70	28.84
Volatile matter, db.	55.27	67.14	61.89	52.78	58.97	61.23
Fixed carbon, db.	8.45	9.20	1.70	15.09	12.33	9.93
C, db.	30.02	39.29	43.31	37.28	-	39.03
H, db.	4.58	5.62	6.94	5.50	-	5.42
N, db.	5.41	7.68	1.63	5.67	-	6.79
S, db.	0.51	0.61	0.11	1.01	-	0.72
O, db.	23.19	23.14	11.60	17.94	-	19.20

ar. - as received, db. – dry basis

3.2 Major ash-forming elements

The content of major ash forming elements in dry sludge samples is shown in Fig. 1 and 2. It can be seen from the figures that the Si content was the highest among all elements for both sludge types. Yet, it was higher in SS (270-400 g/kg) than in DS (150-300 g/kg). Similar concentrations of Na (20 - 30 g/kg) and K (3 – 9 g/kg) in all sludge samples were observed. Generally, comparable concentrations of P and S was observed for both types of sludge (12 - 18 g/kg and 1 - 4 g/kg, respectively). On average, the content of Al was similar in all SS samples (around 20 g/kg) but significant difference were observed in DS concentrations. The highest Al concentration of 40 g/kg was in DS-1 while only 10 and 5 g/kg in DS-2 and DS-3-DAF. The Ca content was similar in SS samples (around 20 g/kg). DS samples, however, showed substantial differences with around 15 g/kg in DS-1 and DS-2 versus 50 g/kg in DS-3-DAF. Overall, a higher content of Fe was observed in SS, but there were also large differences between particular samples within the two tested groups. The Fe content was 5 g/kg in SS-1 and SS-2 and 25 g/kg in SS-4 compared to 0.6 g/kg in DS-2 and DS-3-DAF and 3 g/kg in DS-1. Slightly higher content of Mg was observed in SS samples than in DS samples (3 - 8 vs 0.4 - 3 g/kg, respectively).

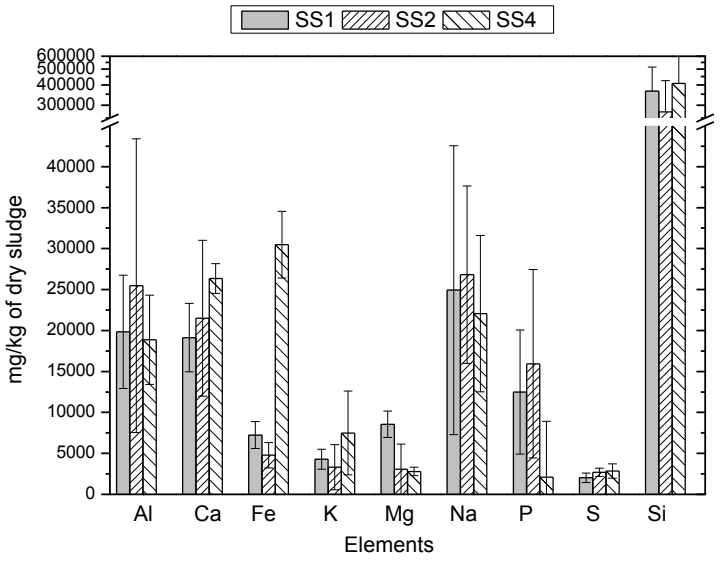

Fig 1. Major elements in municipal wastewater sludge

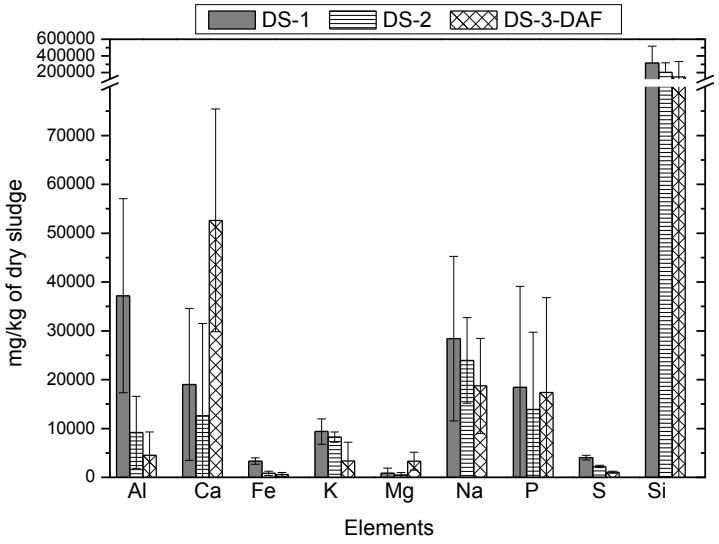

Fig 2. Major elements in sludge from wastewater treatment plants in milk processing factories.

3.3 Minor ash-forming elements

The content of minor ash forming elements in dry sludge samples is shown in Fig. 3 and 4. It can be seen from the figures that in general the content of heavy metals is higher in SS. In particular, the content of titanium, zinc, copper, barium and manganese in SS is about four times of that in DS. Also, a higher Cr and Pb content was detected in SS than in DS (20 - 160 vs 5 – 9 mg/kg, and 50-160 vs 15 - 70 mg/kg, respectively). Likewise, a higher concentration of Ni and V was observed in SS than in DS (12 - 100 vs 5 – 9 mg/kg and 9-20 vs 5 mg/kg, respectively). Whereas, similar concentrations of Hg (10 - 40 mg/kg) with trace amounts of Se (1.5 - 5 mg/kg) and Sb (0.6 - 5 mg/kg) were measured in all sludge samples. SS samples contained trace amounts of arsenic, cobalt and cadmium. There was no cadmium observed in DS samples but in DS-1 and DS-2 trace amounts of arsenic and cobalt were found.

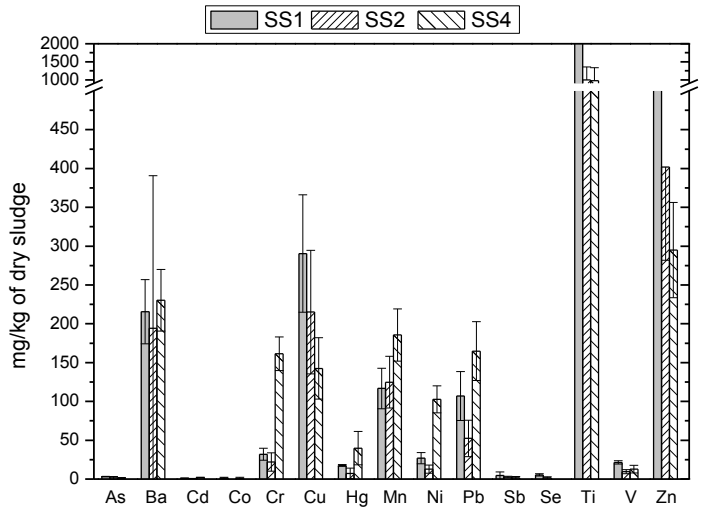

Fig. 3 Minor elements in municipal wastewater sludge.

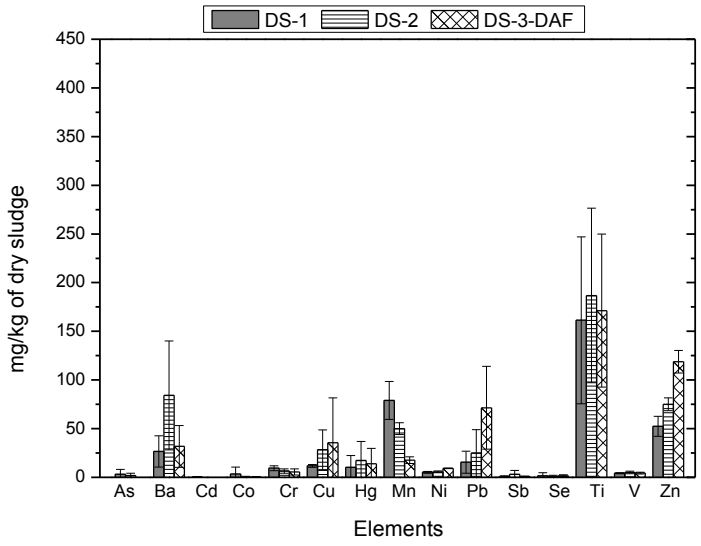

Fig 4. Minor elements in sludge from waste water treatment plants in milk processing factories.

3.4 Retention of major and minor elements in pyrolysis char

The average values and distribution of the pyrolysis products obtained in laboratory scale experiments are reported in Table 3. Owing to relatively high initial ash content, pyrolysis of all sludge types produced a significant quantity of pyrolysis solids comprising from 30 to 40 % (DS) and from 36 to 45 % (SS) of the initial dry sludge mass. For SS samples, the remaining 60 % was more or less equally split between liquid (26 and 33 %) and gaseous (30 %) products. Relatively high yield of liquid fraction was obtained for DS-1 and DS-2 at 37 % while the gas fraction was 32 and 22 %, respectively. The partitioning of solid and liquid pyrolysis products showed slight differences for DS-3-DAF, having less solids (15 %) while the gas fraction was the highest among all tested sludge samples (47 %).

The experimental uncertainty in the char yield was low because the sludge sample and char were measured directly. In contrast the liquid yield had a greater uncertainty. Even though the whole experimental apparatus was weighed before and after pyrolysis in order to obtain the mass of the liquid fraction there was always some oil condensed in the gas sampling bags. This indicates that some pyrolysis products escaped the apparatus as vapours or aerosols. Thus, based on the conservation of mass, the measured liquid fraction should be considered the minimum. Consequently, as the gas yield is calculated by the difference between the solid and the liquid pyrolysis products and the initial sample mass, the gas yield should be considered the maximum value.

Table 3. Average product distribution from pyrolysis of sludge samples at 700°C for 10 min.

Sample	Solid product, wt. %	Liquid yield, wt. %	Gas yield, wt. %
DS-1	30.5 +/- 0.2	37.2	32.3
DS-2	39.7 +/- 0.5	37.9	22.5
DS-3-DAF	37.5 +/- 2.6	14.7	47.8
SS-1	44.8 +/- 0.1	25.7	29.5
SS-2	40.2 +/- 2.4	-	-
SS-4	36.5 +/- 0.9	33.2	30.3

Results of proximate and ultimate analysis of the solid pyrolysis products are presented in Table 4. The solid product from pyrolysis most often are called chars, but when the ash content in solids is over 50% according to nomenclature intruded by European Biochar Certificate, term pyrogenic carbonaceous material is used instead.

The solid products, from SS and DS pyrolysis consisted mainly of ash at about 66 - 82 wt. %, therefore the term pyrogenic carbonaceous material is also used further in the discussion.

For DS-1, DS-2 and SS-1 the char (pyrogenic solids) contained a substantial amount of fixed carbon, 20 and 27 wt. %, respectively. This observation, is in line with findings of Shao et al. [20] who reported that some metal oxides (CaO, Fe_2O_3 and ZnO) tend to inhibit the decomposition of organic matter, causing greater formation of solid residue. All these oxides were present in SS and DS.

The volatile matter content of chars (pyrogenic solids) from DS-1, DS-2 and SS-1 was low at about 5 wt. % implying that almost complete decomposition of the organic matter occurred in the fixed bed reactor at 700°C and a residence time of 10 min. On the other hand, the volatile matter content in DS-3-DAF and SS-2 solids was 15 wt. % and this suggests that decomposition of DAF-S2 was not accomplished at 700°C and a fraction of organic matter was still un-released from the solid matrix.

Only 9 -12 % of the initial nitrogen content in the sludge samples was retained in the char. It can be concluded that the majority of the nitrogen was released via gaseous components or was retained in the liquid fraction.

Table 4. Proximate and ultimate properties of pyrolysis chars (pyrogenic solids) (700°C for 10 min.)

Properties, wt. % db.	DS-1	DS- 2	DS-3-DAF	SS-1	SS-2
Ash content	75.47	66.32	81.88	69.4	71.21
Volatile matter	4.05	6.77	14.48	3.2	16.02
Fixed carbon	20.48	26.91	3.63	27.4	12.77
C, db.	20.00	27.48	10.11	11.7	8.56
H, db.	0.40	0.31	0.55	28.68	28.11
N, db.	1.98	2.46	0.39	0.09	0.54
S, db.	0.36	0.41	0.04	1.94	2.67
O, db.	0.55	0.99	7.07	0.41	0.57

The results for the retention of major elements in the char (pyrogenic solids) are presented in Fig. 5 and 6. On average over 70 % of initial fraction of all major elements were retained in the char (pyrogenic solids) for SS and DS except for S. However, diverse trends can be seen when looking at individual SS and DS samples. For example, fraction of Al, K, Na, P and Si seems to be released with the vapour phase during pyrolysis or the mass balance closer is pure in these cases due to errors associated with analytical procedure. In contrast, from 50 to 70 % of sulphur was retained in the char. Similar findings were reported in literature [9].

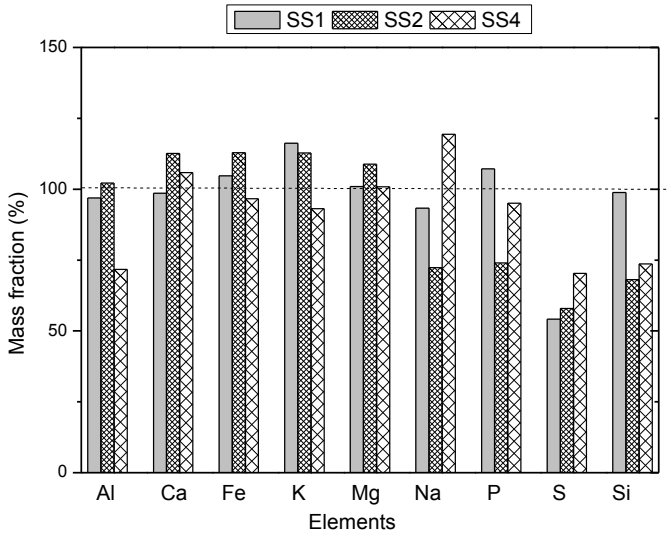

Fig 5. Major element retention in SS derived pyrolysis char (dry basis).

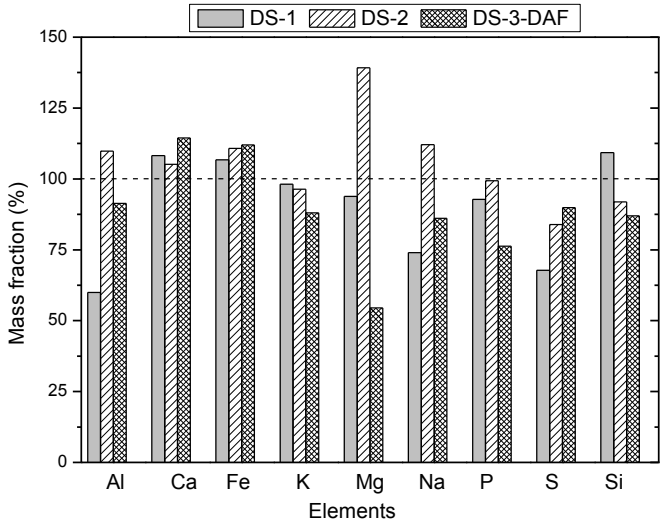

Fig 6. Major element retention in DS derived pyrolysis char (dry basis).

For the minor elements Cu, Cr, Mn, Ni, Pb, Ti, and Zn, most were retained in the char (pyrogenic solids) of both sludge types (Fig 7 and 8). Similar observations for Cu, Cr, Ni, Pb and Zn have been reported [11]. Hen et al. [21] observed that only about 10% of Pb was volatilised during slow pyrolysis at 923K. On the other hand, only from 25 to 50% of Cd, Sb and Se was conserved in the char (pyrogenic solids). Dong et al. [22] found that cadmium was more volatile in the reducing atmosphere of the pyrolysis process. Significant release of Se during pyrolysis at temperatures above 550°C was reported [23,4].

As the most volatile trace element [23], mercury was mostly in the gaseous product, despite significant amounts retained in the char (pyrogenic solids) of SS-1. Arsenic can also be a mobile element in sludge but the presence of CaO and Fe_2O_3 acts to minimise emission through formation of stable As compounds [21].

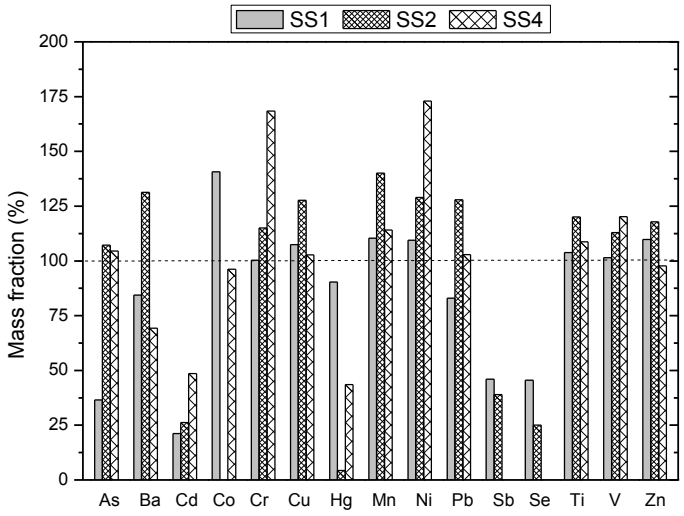

Fig 7. Minor element retention in SS derived pyrolysis char (dry basis).

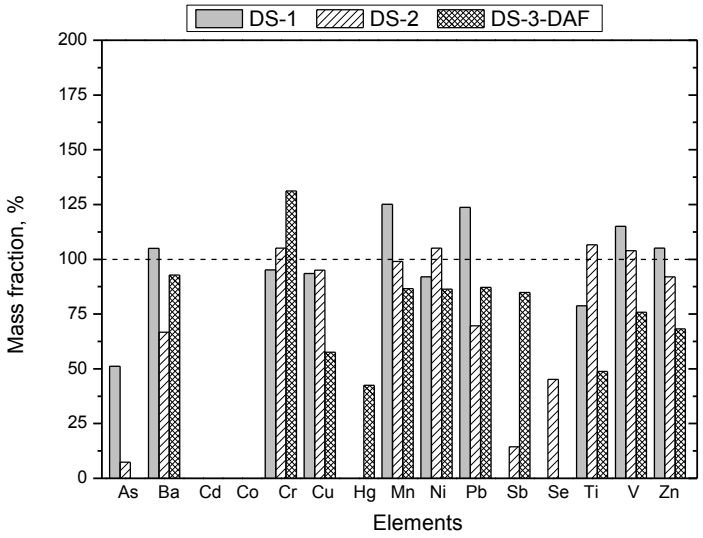

Fig 8. Minor element retention in DS derived pyrolysis char (dry basis).

3.5 Distribution of ash forming elements between solid and liquid products

The content of ash forming elements in the liquid pyrolysis products was also determined for two samples, SS-1 and DS-2. This was done to investigate the distribution of major and minor compounds between pyrolysis products.

The liquid fraction obtained from pyrolysis was dark brown in colour and consisted of two visible phases, the oil and aqueous fraction, and were easy to separate. The latter contained water and certain hydrosoluble organic compounds while the oil contained the organic fraction. As some pyrolysis products escaped the apparatus as aerosols or vapours there is uncertainty associated with measurements of total mas of liquids generated during pyrolysis thus the results presented in Fig 9, 10, 11 and 12 should be viewed as qualitative. In the SS-1 pyrolysis oil some quantities of Al, K, Na, S and Si were detected. The same elements were detected in aqueous fraction together with some Ca and Mg. Likewise in the DS-2 pyrolysis oil substantial amounts of Al, Na, S and Si were also detected. In contrast to SS-1 a small amount of K was measured in DS-2 oil. The DS-2 oil contained also small amounts of elements, which are not volatile, like Ca, Fe and Mg. Most major elements were detected in DS-2 aqueous fraction with the exception of Ca and P. Zhang et al. [9] reported three types of sulphur-containing compounds found in pyrolysis oil (tar); these are aromatic-S, aliphatic-S and thiophene-S.

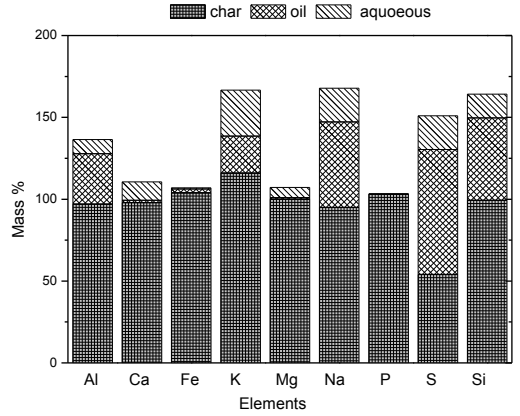

Fig. 9. Distribution of major elements between SS-1 pyrolysis products (wet basis).

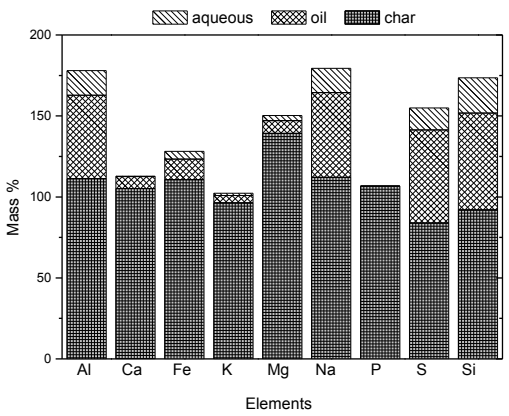

Fig. 10. Distribution of major elements between DS-2 pyrolysis products (wet basis).

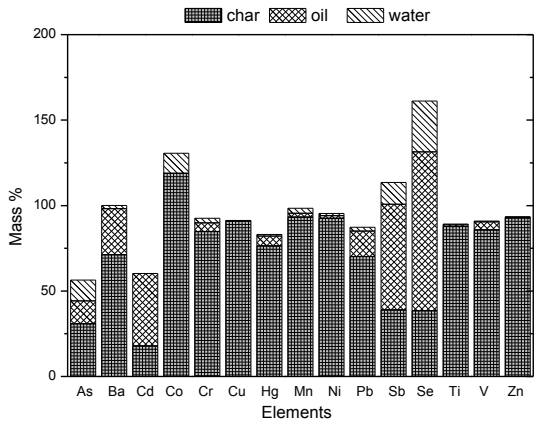

Fig. 11. Distribution of minor elements between SS-1 pyrolysis products (wet basis).

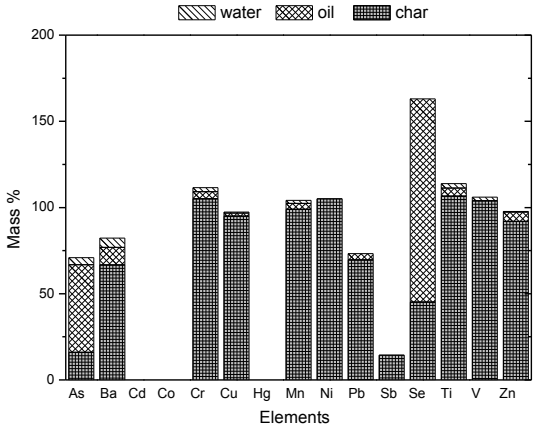

Fig. 12. Distribution of minor elements between DS-2 pyrolysis products (wet basis).

Considerable amounts of Se, Sb, Cd, Ba and As were detected together with some Pb, Hg and Cr in SS-1 pyrolysis oil. The same elements in smaller quantities were detected in aqueous fraction. In the dairy sludge pyrolysis oil substantial amounts of only three elements were detected, namely Se, As and Ba. The DS-2 oil contained also small amounts of Cr, Cu, Mn, Pb, Ti and Zn. Minimal amounts of As, Ba, Cr, Cu, Mn, and Ti were also detected in DS-2 aqueous fraction.

There were trace amounts of almost all tested elements in the pyrolysis liquid products, even for non-volatile elements, which could come from small particles of feedstock elutriated from the bed of material during rapid release of volatiles causing particle fractionation.

4. Conclusions

In this study, properties of sludge from municipal wastewater treatment plants were compared with sludge from treatment of wastewater in milk processing factories in terms of proximate and ultimate properties and content of major and minor ash forming elements.

On a dry basis, sewage sludge (SS) samples from three different plants had similar properties while there were substantial difference in the properties between the dairy sludge (DS) samples. Both sludge types had high ash content, SS about 30 wt. % while DS from 25 to 36 wt. %. The concentration of P, K, Na and S was similar in SS and DS, while the content of Si and Mg was higher in SS. There were significant differences in concentration of Al, Ca and Fe between samples within the two tested groups. In general, the heavy metal content was much lower in the DS, in particular Cr, Pb, Ni and V. Content of Ti, Zn, Cu, Ba, and Mn in SS was about four times greater than that in DS. Similar concentrations of Hg, Se and Sb were observed in all sludge samples. Trace amounts of As and Co were detected in all SS and some DS samples. There was no Cd in DS samples in contrast to SS.

For an intermediate pyrolysis at 700°C in a fixed bed reactor, the distribution of pyrolysis products varies between DS and SS. Owing to relatively high initial ash content, both sludge types produced a significant quantity of pyrolysis solids from 30 to 40 % (DS) and from 36 to 45 % (SS) of the initial residue mass. Distribution of major elements between pyrolysis products was similar for DS and SS, with Ca, Mg, Fe, P, Si, Al, Na and K predominantly retained in pyrolysis chars (pyrogenic solids). However, substantial quantities of Al, K, Na and Si were detected in pyrolysis oil and in the aqueous fraction. From 50 to 70 % of S was retained in the solids with significant quantity captured in the liquid fraction. The heavy metals and trace elements were mainly retained in the pyrolysis chars with the exception of As, Ba, Cd, Se, Sb and Pb, which were also detected in the liquid products.

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