SEWAGE SLUDGE: CHARACTERISTICS AND RECOVERY OPTIONS

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Abstract

In this paper, an overview on sewage sludge characteristics and recovery routes is presented. Starting from an analysis of typical sewage sludge characteristics as found in literature, the most promising disposal options are presented. A focus on incinerated sewage sludge ash (ISSA) follows. Most of the authors agree on considering pyrolysis and gasification as the most viable treatments for sludge in the near future. For this reason, the last two chapters offer a brief description of these two processes and their products.

Sewage sludge

- *Characteristics*

Sewage sludge is a kind of waste coming from municipal wastewater treatment plants. In these facilities, high quantities of water are treated every day to eliminate bacteria, viruses and pollutants. As main output, these plants produce treated water and sewage sludge.

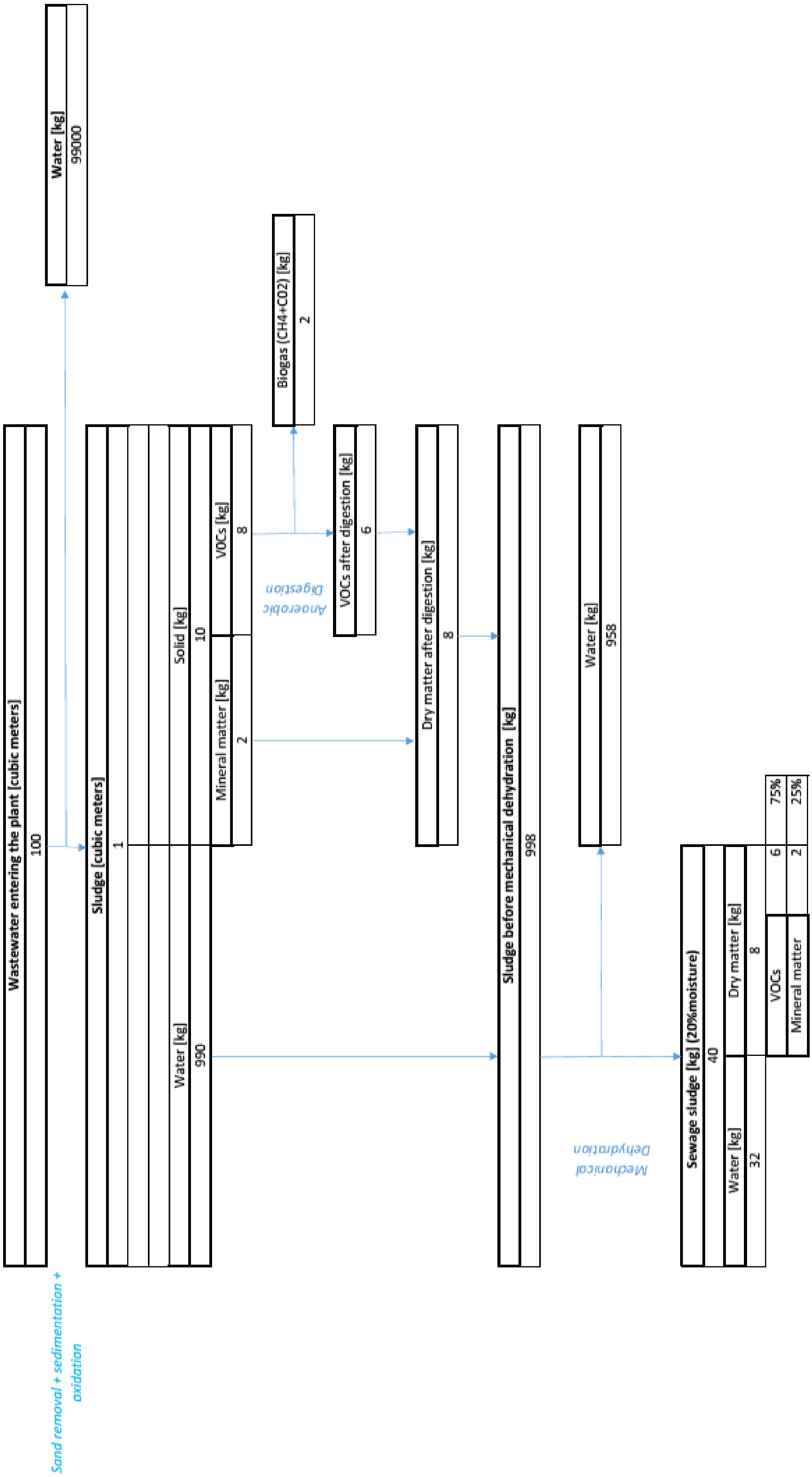
A qualitative example in Fig.1 shows the main steps of the process followed by municipal wastewater treatment plants in Bologna district (Italy). The calculations refer to 100 cubic meters of wastewater entering the municipal treatment plant.

Sludge, which constitutes 1% of wastewater entering the plant, is digested anaerobically and dehydrated. Sewage sludge, at the outlet after mechanical drying, is made of approximately 80% moisture and 20% dry matter.

The management of this product has become a serious problem in Europe over the last years because of legislation and environmental issues. Typical destinations for sewage sludge were agriculture, forestry, incineration, land building or landfills, but most of them have been banned or limited by recent EU and local laws.

Sludge constituents are organic and inorganic compounds, including traces of heavy metals such as chromium, zinc, mercury, lead, nickel, cadmium and copper. These elements restrict the use of sludge in agriculture, because their accumulation is harmful to the environment and particularly to the food chain.

Figure 2 and Figure 3 are the result of a comparison between various sewage sludge characteristics data found in literature [5, 24, 25, 34, 35, 36, 37, 38, 39, 40].



Wastewater entering the plant [cubic meters]
100
Sand removal + sedimentation + oxidation
Water [kg]
99000
Sludge [cubic meters]
1
Solid [kg]
10
Water [kg]
990
VOCs [kg]
8
Mineral matter [kg]
2
Anaerobic Digestion
Biogas (CH4+CO2) [kg]
2
VOCs after digestion [kg]
6
Dry matter after digestion [kg]
8
Sludge before mechanical dehydration [kg]
998
Mechanical Dehydration
Water [kg]
958
Sewage sludge [kg] [20%moisture]
40
Water [kg]
32
Dry matter [kg]
8
VOCs
6
75%
Mineral matter
2
25%

Figure 1

	MIN	MAX	MEAN
Proximate analysis	% DB		
Moisture			*80,00*
Volatiles	38,30	73,70	56,63
Ash	24,08	52,00	35,91
Fixed carbon	0,30	9,41	7,47

Figure 2

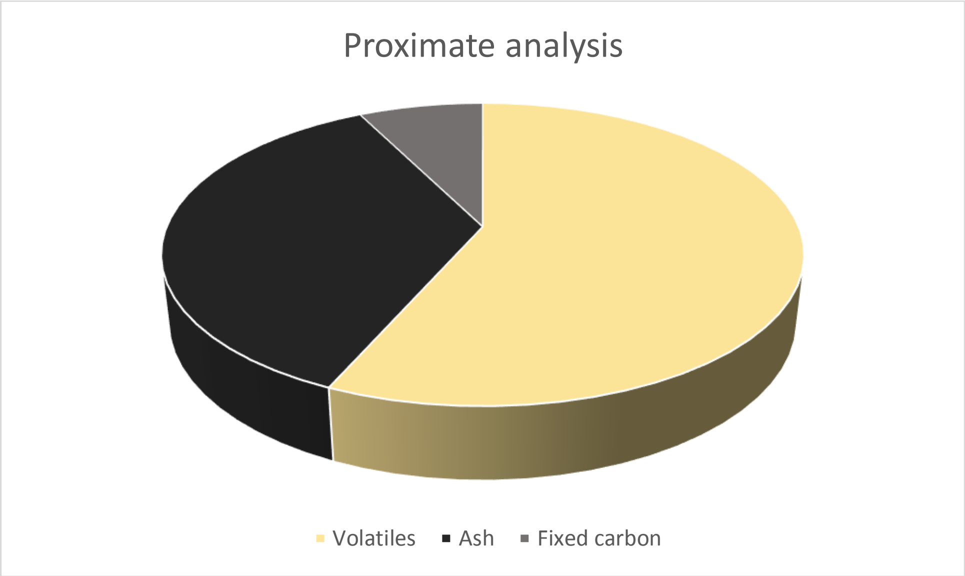


Figure 3

Authors made their measures on samples with different moisture contents, reporting the data on dry basis (DB). A typical value of 80% has been taken as indicative for moisture content in Figure 2. Proximate analysis shows that most of the sample is made of volatiles, and the total ash content settles around 36%. This subdivision justifies the focus that has been put by researchers in the last years on combustion and gasification processes. Sludge can be treated as a fuel, with a double income: the production of energy and the reduction in the dry matter to be disposed. Typical Higher Heating Values of the samples find in literature settle between 12000 and 16000 kJ/kg, as shown in Figure 4 and Figure 5, reporting the results for ultimate analysis as found in literature.

As mentioned before, analysis of sewage sludge cannot be limited to this, because of the complexity of the mixture. Minor trace elements and elemental concentrations offer a more detailed view on substances contained in the sludge.

Sewage sludge contains a relatively high quantity of heavy metals, as shown in Figure 6 and Figure 7. From a comparison between minimum and maximum values it comes clear that concentrations are strongly variable depending on sewage sludge origin.

Lead, zinc and copper are present in high quantities, but other heavy metal traces such as mercury cannot be neglected due to their harmful potential.

	MIN	**MAX**	**MEAN**
Ultimate Analysis	% DB		
C	23,10	42,30	32,51
H	3,10	6,00	4,49
N	3,20	8,30	4,85
O	17,70	34,00	22,53
S	0,44	19,10	0,87
HHV [kJ/kg]	8900,00	21100,00	13292,86

Figure 4

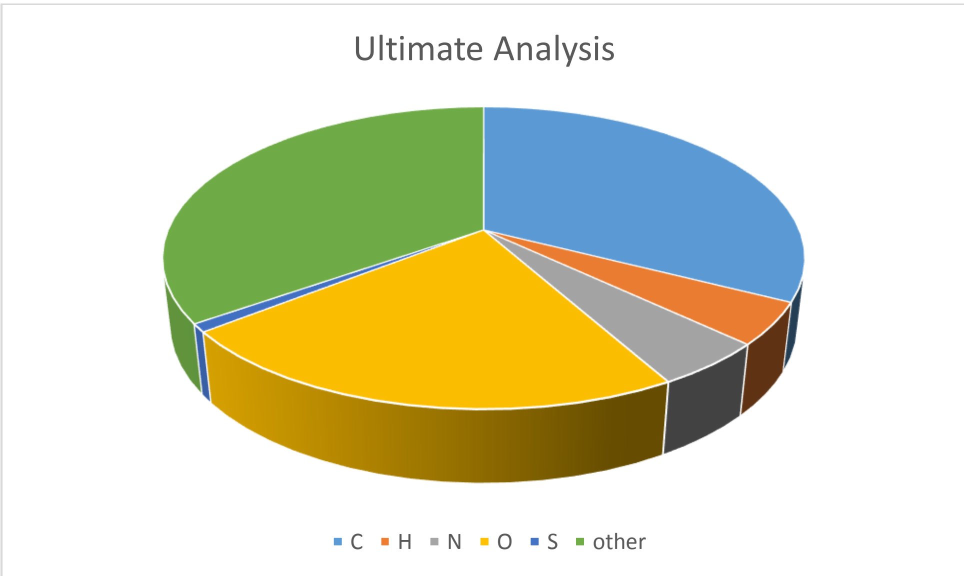


Figure 5

	MIN	MAX	MEAN
Minor trace elements	mg/kg DB		
Pb	47,00	246,00	141,75
Hg	0,92	3,00	1,79
Mn	82,00	239,00	178,33
Ni	13,20	42,70	29,73
Zn	662,00	1020,00	867,25
Co	3,50	5,00	4,25
Cd	1,36	3,00	2,42
Cr	39,00	163,00	102,50
Cu	143,00	309,00	215,75
Fe	9900,00	28911,00	18737,00

Figure 6

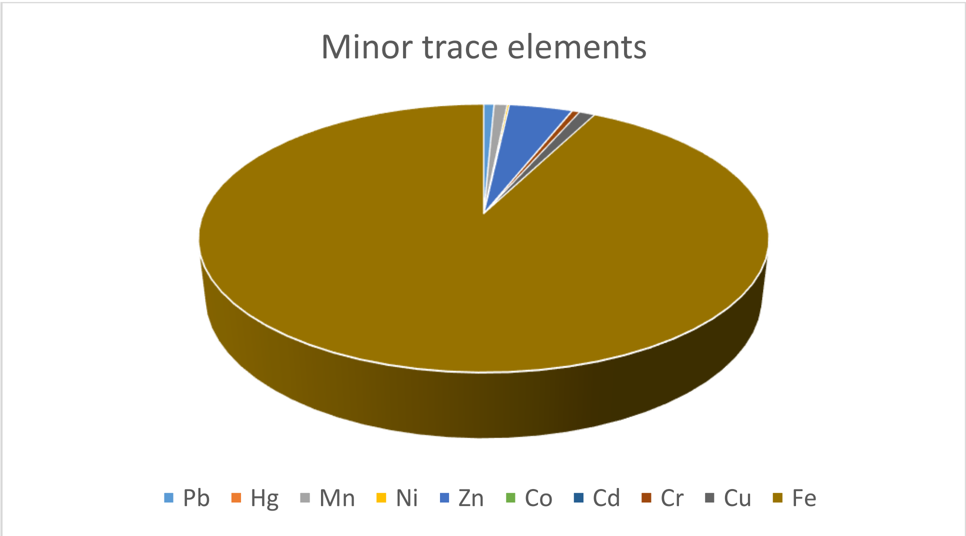


Figure 7

Elemental concentrations	wt% DB
P	3,77
Si	2,63
Ca	2,35
Fe	1,89
K	1,56
S	1,26
Al	1,14
Cu	0,97
Mg	0,92
Zn	0,37
Na	0,21
Sn	0,16
Ti	0,13
Cl	0,11
Other	82,53

Figure 8

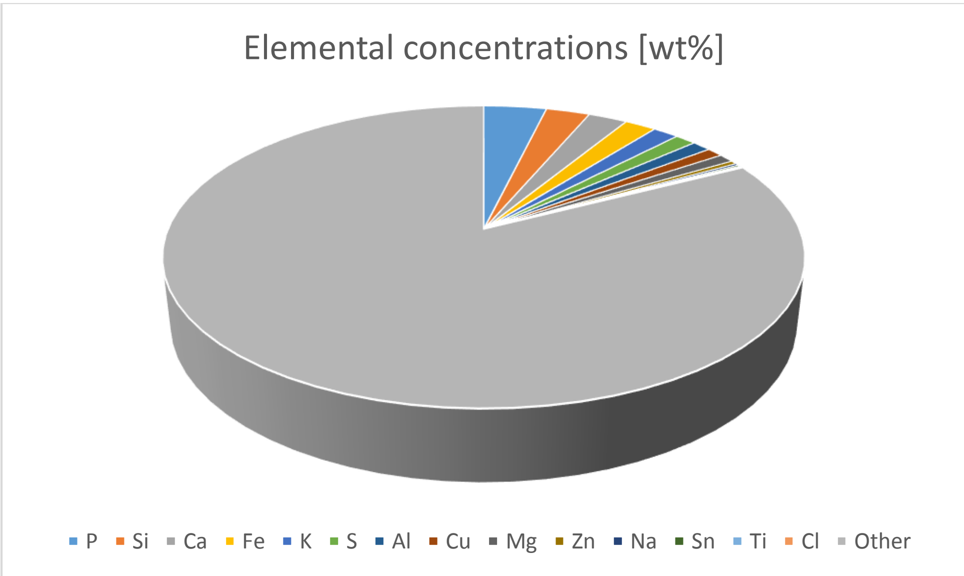


Figure 9

Some of the elements represented in Figure 8 and Figure 9, which report elemental concentrations weight percentiles (dry basis) as reported by Gao et al. [26], are worth mentioning. In fact, phosphor and potassium have both a high fertilizer value, while silica suggests good properties for soil stabilization applications. These characteristics offer good opportunities for the recovery of fertilizers and construction materials from sewage sludge, as will be explained in following paragraphs.

- *Raw materials extraction and recovery routes*

Sewage sludge disposal choices for different countries are shown in Figure 10 [9] and Figure 11 [3]. Overall EU, EC report "Environmental, economic and social impacts of the use of sewage sludge on land" (2008) estimates that an average of 14% dry solids is landfilled, while a 42% is spread on land for agriculture. At a first glance to Figure 10, this trend seems to be confirmed worldwide, while most of the countries settle on the graph line between landfill and agricultural use.

The use of sewage sludge to agricultural land has been considered for a long time as the best practical environmental option because of its high fertilizer value. Sludge disposal to land is regulated by EU Sludge Directive 86/278/EC, but many countries have settled stronger limits because of public concerns associated mainly with accumulation of heavy metals in soils. Moreover, the Landfill Directive 1999/31/EC defined waste capable of undergoing anaerobic or aerobic decomposition as unacceptable in landfill. For these reasons, most of the countries with low levels of land spreading, see Figure 11 (which is referred to year 2009), are the ones who decided to invest significantly in incineration over last years. This option has gradually become the preferred one in most industrialized European countries. For this reason, next chapter will be entirely focused on incinerated sewage sludge ash (ISSA) characteristics and disposal practices.

Due to the high volumes involved and the impact on local and global economies, many efforts have been carried out to find alternative solution for sludge disposal.

Most of international studies focus on sludge pyrolysis and gasification as alternative to standard incineration processes. These technologies characteristics and their products will be presented in third chapter of this work. Here a brief overview is presented about two alternatives to common disposal routes. Despite most of the processes described are still not economically feasible, they may represent a valid alternative for the near future.

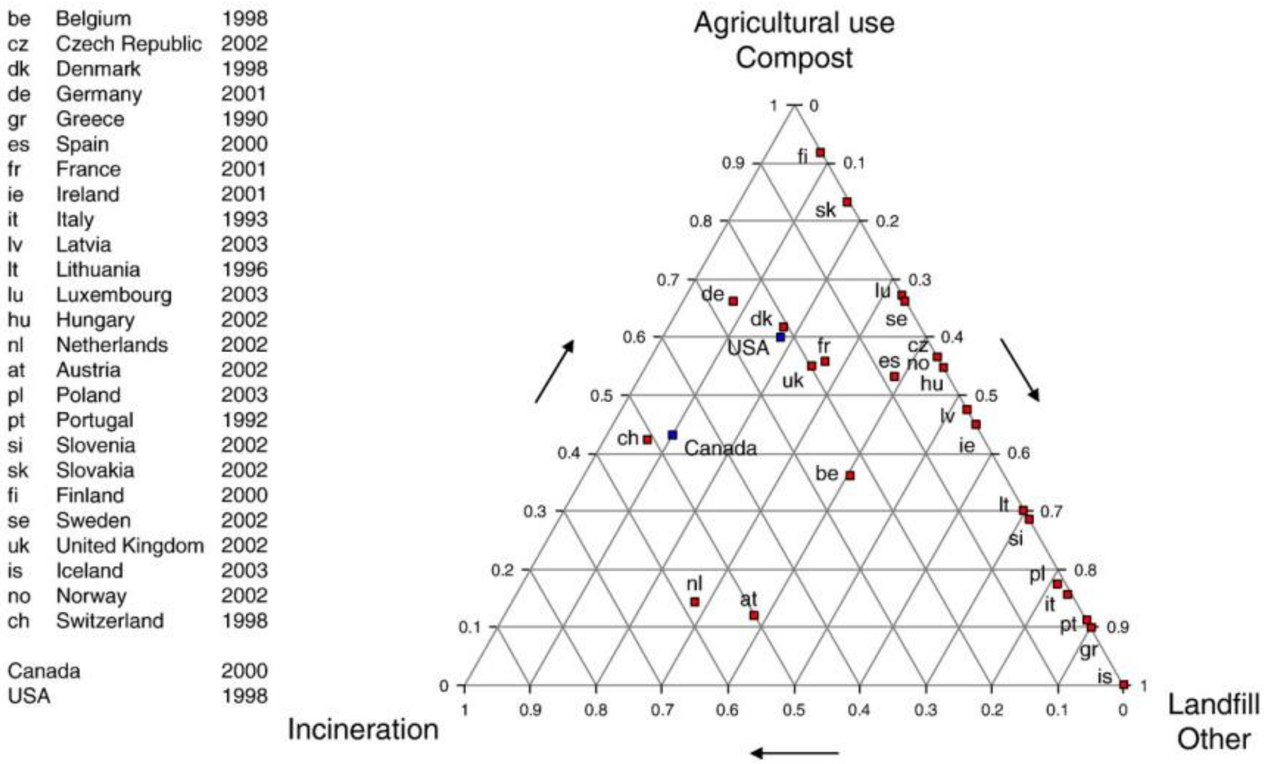


Figure 10

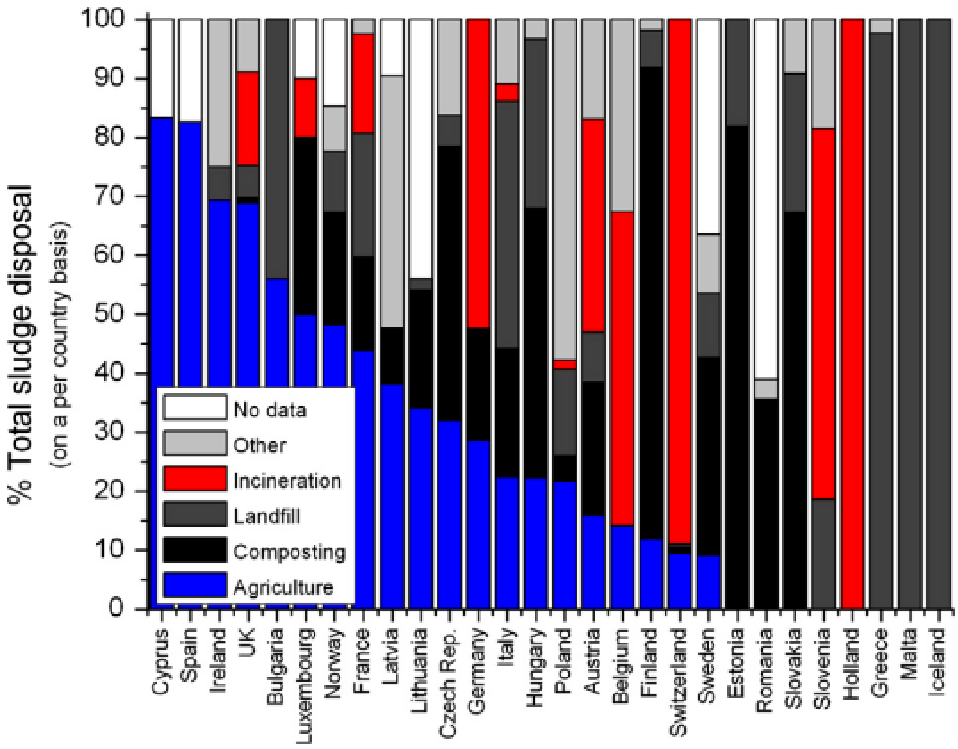


Figure 11

Nutrient recovery

Chemical analysis of sewage sludge shows its high content in potentially valuable phosphorus.

Phosphate demand is high for the manufacture of fertilizers, animal feed and detergents. The number of phosphate geological reserves is limited, and once phosphor enters rivers or sees is not economically recoverable anymore. At current consumption rates, only 50-100 years of economically viable phosphate reserves are estimated to remain.

Recently, methods for phosphorus recovery from sewage sludge via crystallization have been developed. Combination of thermo-chemical treatments allow the phosphorus solubilization process, which releases the element to a supernatant.

These processes produce mainly calcium phosphate and magnesium ammonium phosphate. The first chemical is readily recyclable in industries, since it is the same substance found in mined phosphate ore. The second one, which is generally referred to as struvite, is a good fertilizer due to its slow release properties, and is applicable directly on the soil.

Most of these methods are still studied only at laboratory or pilot scale, because of their high energy and economic cost. In fact, the cost of phosphorus recovery is estimated as 22 times higher than the cost of mined phosphate ore. Anyway, on one hand the progressive exhaustion of phosphorus mines will result in a global rise in ore price in next decades. On the other hand, limits on sewage sludge landfilling will rise sludge disposal cost. This should result in a higher industrial appeal for these processes over upcoming decades.

Construction material

Dried sludge can be converted into artificial lightweight aggregates, slags or bricks for the construction industry. Different properties and destinations for these materials depend on different process variables and operating conditions.

As of the use of dewatered sludge, the production of Portland cement injecting the sludge directly into cement klins seems the most appealing one. The major elements present in Portland cement are in fact Ca, Si, Al and Fe, which compare reasonably well to the elements present in sewage sludge.

Sludge can be exploited in construction industry in other different forms such as dried sludge powder or incinerated ash, as will be seen in next chapter.

Many technically feasible processes have been studied and tested, but most of the techniques are not economically viable because of a high production cost, if compared to market price.

<u>Sewage sludge ash (ISSA)</u>

- *<u>Characteristics</u>*

The output of sewage sludge incineration process is Incinerated Sewage Sludge Ash (ISSA), which characteristics are slightly different from the ones seen for sewage sludge.

Cyr et al [3] provide mean values for ISSA chemical analysis as found in literature (Figure 12 and Figure 13).

Oxide	**%**
SiO2	36,1
Al2O3	14,2
Fe2O3	9,2
CaO	14,8
P2O5	11,6
SO3	2,8
Na2O	0,9
K2O	1,3
TiO2	1,1
MgO	2,4
MnO	0,3
LOI	6,1

Elements	[mg/kg]
As	87
Ba	4142
Cd	20
Co	39
Cr	452
Cu	1962
Ni	671
Pb	600
Sb	35
Sn	400
Sr	539
V	35
Zn	3512

Figure 12

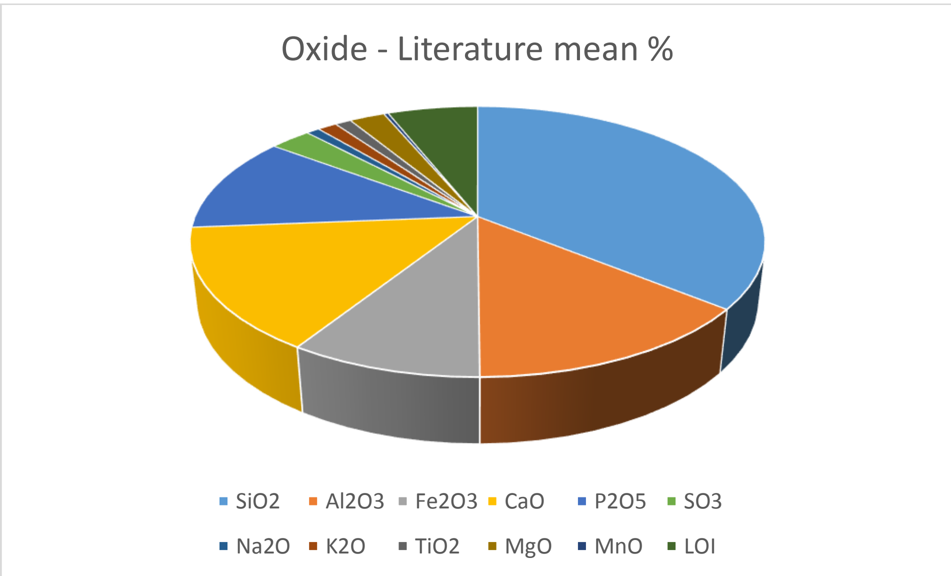


Figure 13

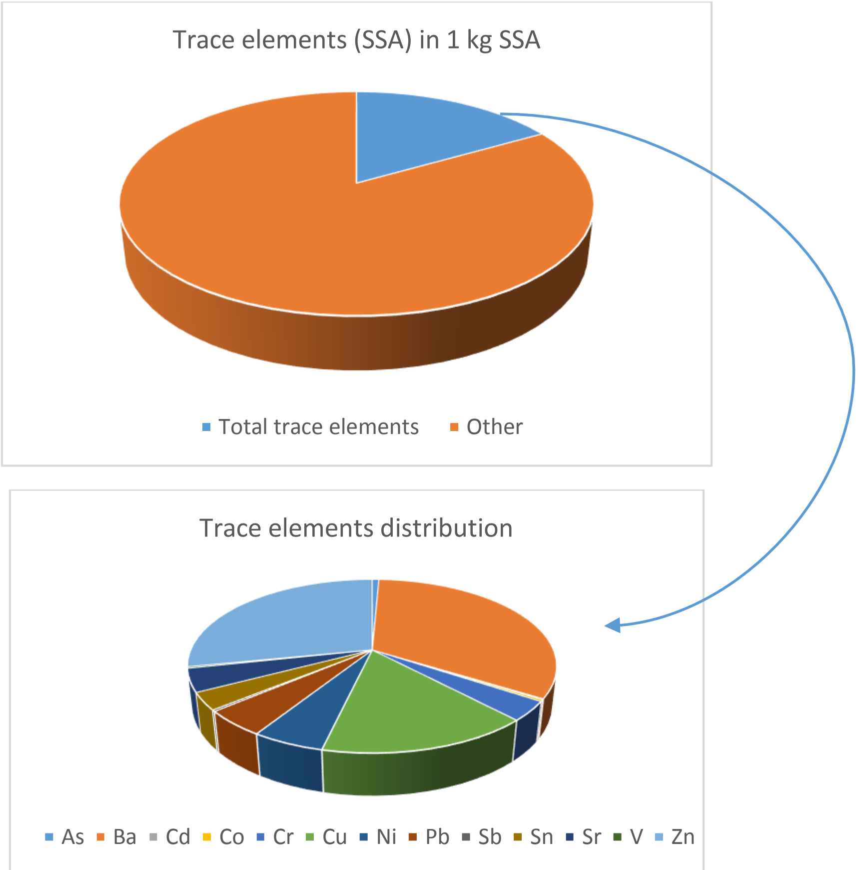


Figure 14

As for common sewage sludge, the major elements in ISSA are silica, aluminium, calcium, iron and phosphor. The difference in trace elements composition is due to the partial or complete volatilization of metals such as mercury, cadmium, antimony and lead during combustion. However, these metals presence depends on combustion process and is highly variable in literature.

Ash mean particle diameters range from 8 to 263 µm, with particle sizes ranging from submicron to around 700 µm. The pH of sludge ash can vary between 6 and 12, with a general alkaline behaviour.

- *Raw materials extraction and recovery routes*

ISSA is commonly landfilled with high disposal costs and environmental impact. While this ash is intrinsically absent of water, it can be recycled in more different ways than common sewage sludge (particularly for what concerns the construction industry). Some recycle possibilities alternative to landfill are introduced below.

Sintered materials

Production of sintered materials is favoured by ISSA elemental composition. In fact, during sintering, the formation of a liquid phase highly reduces the temperature and time necessary to create sintered products. Sintering is a step involved in most of the ceramic industry processes. Possibilities for sewage sludge ash recycle involve the production of:

- *Bricks, tiles and pavers*, substituting clay with ISSA
- *Lightweight aggregates* , which reduce concrete density and improve thermal insulation (these materials are high value because of scarcity of natural alternatives)
- *Glass–ceramics*
- *Lightweight aerated cementitious materials*

Phosphate recovery

Options for recovering phosphor from sewage sludge as exits from wastewater treatment plants have high disadvantages due to high water and organic matter content.

ISSA is dry and in form of powder, and this greatly simplifies phosphate extraction processes. Furthermore, incineration does not lower sewage sludge fertilizing potential, while phosphate is thermally stable up to high temperatures. This means, it does not volatilize during incineration at 800-900°C.

Most promising methods for phosphor recovering are recovery by acid leaching, recycling of acid insoluble ISSA residue and thermal methods.

As for processes described for sewage sludge, these methods encounter high energy and chemical costs. Authors suppose they will become more attractive as both phosphate prices and ISSA disposal costs continue to rise.

Other recycling and recovery options

Zhang et al. [27] considered untreated ISSA a good amendent, thanks to some minor trace elements minor nutrients concentration. A focus put on these nutrients solubility and release rates [14] highlights some limits to this solution. Moreover, heavy metal content limits direct application to soil in many countries.

Lin et al. [11, 10] studied the combination of ISSA with $Ca(OH)_2$ or cement for soil stabilization applications. ISSA has also been used as mineral filler in asphalt production replacing limestone [12].

Pyrolysis and gasification

Sewage sludge disposal problems and increasing demands of energy worldwide have increased attentions in thermo-chemical conversion processes of sewage sludge. Depending on the methods used, sludge is converted into bio-fuels in different forms (biogas, bio-tar and bio-char). Most common processes are pyrolysis and gasification. Regarding product distributions, the first technique is aimed to the production of a liquid fuel out of bio-tar, while the second one has biogas as main desired output.

Biogas and bio-tar become energy resources valid to replace fossil fuels. Bio-char is the less valuable product of these processes, but can be converted into solid fuels further reducing the sludge volume and concentrating the heavy metals in the carbonaceous residue.

- *Pyrolisis*

Pyrolysis is the name of the process of thermal degradation of fuel’s chemical molecules in an inert atmosphere. Main factors determining different product distributions and characteristics are process temperature, residence time in the reactor, pressure, turbulence and raw materials’ characteristics. Temperature range vary from 300°C to 900°C and depend on residence time. Optimum process parameters depend on experimental scale and specific technique, but are normally set around 850°C for 2 hours. Products are fixed carbon, ash, bio oils, combustible gases and water vapours.

Process variables differ depending on the final product desired. Even though pyrolysis is generally aimed to the production of liquid products via liquefaction, other two routes optimize the production of solid products (carbonization) or biogas (gasification).

Carbonization method operates at low temperatures (around 300°C) and high residence times. 90 wt.% of original sludge is converted into a solid char.

Liquefaction process requires low residence times, with average temperatures around 425°C and 575°C. Bio oil produced is 30 to 40 wt.% of starting dry sewage sludge sample. Liquid production seems to be linked with reactions involving carboxylic and phenolic compounds of the original sludge.

Gasification technique requires high residence times and temperatures not lower than 650°C. 51 to 66 wt.% of dry sewage sludge can be finally converted into bio-gas.

Stages of decomposition during pyrolysis process are represented in Figure 15

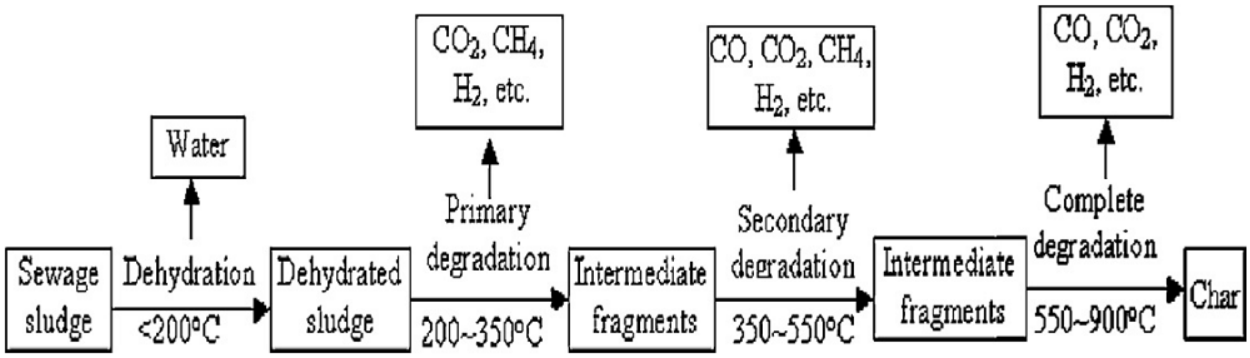


Figure 15

After dehydration, which occurs below 200°C releasing water, three principal stages can be distinguished. A first one, at an average temperature of 250°C, releases mainly methane, carbon dioxide, water and acetic acid. During a second stage, at 350°C hydrocarbons and alcohols appear. Lastly, starting from temperatures around 550°C, the complete degradation of the sludge brings to a final emission of hydrogen, methane, carbon dioxide, hydrocarbons and alcohols.

Most of the biodegradable matter is volatized between 150°C and 400°C, while non-biodegradable organic matter is volatized between 400°C to 550°C.

Pyrolysis product distribution differ significantly depending on the process, the parameters and the sludge characteristics. As an example, some studies are shown below to understand process behaviour ad different temperatures.

Gao et al. [26] studied pyrolysis product distributions for dried sewage sludge at different temperatures with two different heating rates conditions: slow pyrolysis (A) (8°C min^{-1}) and fast pyrolysis (B) (100°C min^{-1}). Results of these experimentations are shown in the Figure 16 and Figure 17, and confirm the increase of gas distribution while temperature rises. On the contrary, solid products reduce as temperature gets higher.

Similar results have been found by Inguazo et al. [20] for anaerobic digested sewage sludge.

Zhang et al. [19] studied high temperature pyrolysis of dried sewage sludge in a free-fall reactor at 1000-1400°C to analyse the possibility of a complete conversion of volatile matter in the sludge to gas product. The diagrams resulting from this study (Figure 18 and Figure 19) show a global increase in gas distribution up to 1200°C, and a simultaneous slow disappear of the tar fraction. Then, from 1300°C on, char and gas distributions remain approximately stable. For what concerns the heating value, as temperature rises it gets rapidly lower, dropping from a maximum around 16 MJ/Nm^3 at 1000°C to a minimum settled around 9 16 MJ/Nm^3 from 1300°C on.

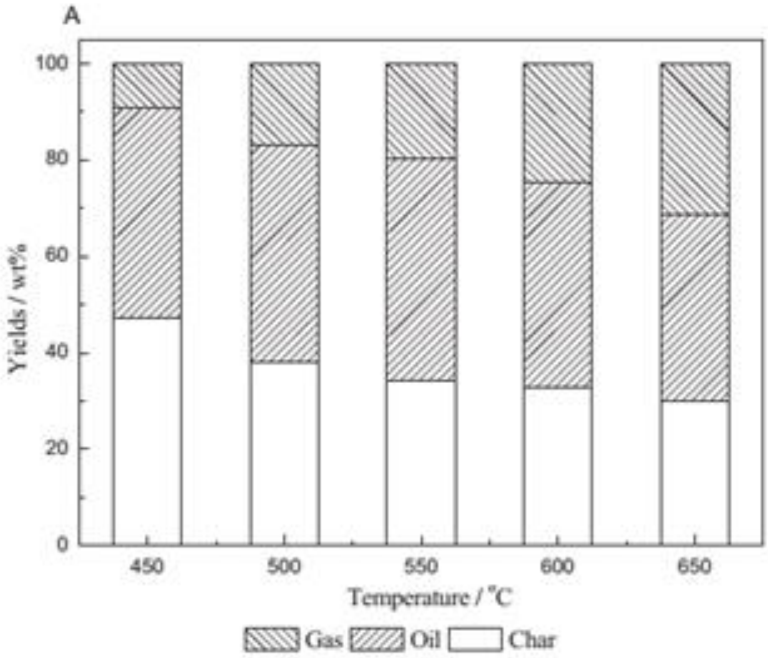


Figure 16

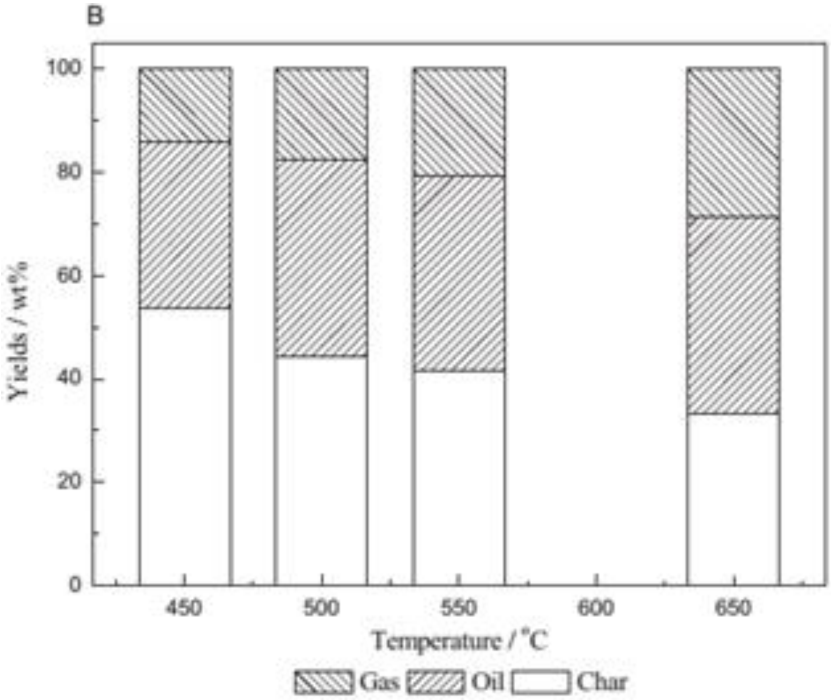
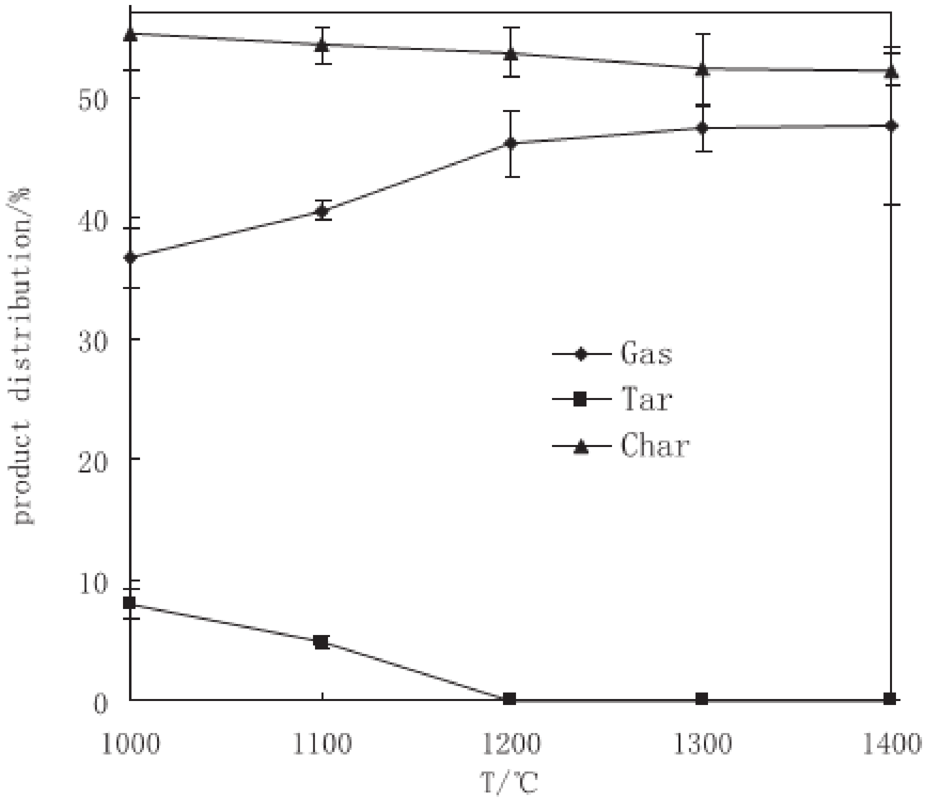
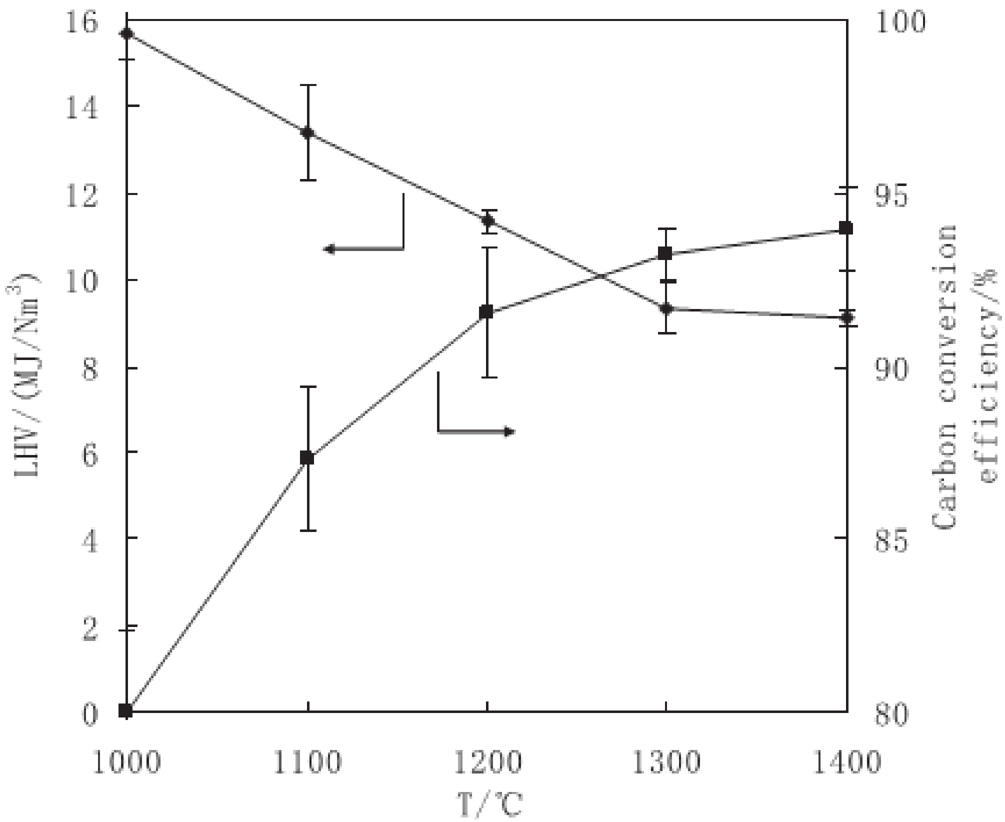


Figure 17



product distribution/%
50
40
30
20
10
0
1000
1100
1200
1300
1400
T/℃
Gas
Tar
Char

Figure 18



LHV/(MJ/Nm^3)
16
14
12
10
8
6
4
2
0
100
95
90
85
80
Carbon conversion efficiency/%
1000
1100
1200
1300
1400
T/℃

Figure 19

- *Gasification*

Gasification process converts carbonaceous materials in the sewage sludge into fuel through a process involving partial oxidation of the sludge in a reducing atmosphere. This conversion takes place in the presence of steam or air at temperatures ranging from 800 to 1400°C. Inorganic matter in the sludge indeed is converted into a glassy solid material called slag, and halogens are converted into acid halides. Interest in this process is based on the fact that syngas produced is usable in gas turbines for production of electricity. Steam gasification is generally preferred because it favours hydrogen distribution, and improves syngas quality and heating value.

An energy input is necessary to start the gasification process, because some of the main reactions necessary to start the process are endothermic. The total process is actually energetically self-sustaining at steady-state conditions. Main chemical reactions, as listed by Fericelli [29] are shown in Figure 20:

Chemical reaction	**Thermal process**
C (fuel) + $O_2 \rightarrow CO_2$ + heat	Exothermic
C + H_2O (steam) $\rightarrow$ CO + H_2	Endothermic
C + $CO_2 \rightarrow$ 2CO	Endothermic
C + $2H_2 \rightarrow CH_4$	Exothermic
CO + $H_2O \rightarrow CO_2 + H_2$	Exothermic
CO + $3H_2 \rightarrow CH_4 + H_2O$	Exothermic

Figure 20

Sewage sludge gasification can be divided in three stages, as described in Figure 21 by Manara et al. [5] : drying, pyrolysis and gasification (thermal).

Drying stage takes place in a temperature range around 70-200°C, and is overall endothermic. During this stage, water content of sludge is removed and depending on the type of gasifier dry solid content output is between 85-93%.

After sludge drying temperature rises to 350-500°C, and pyrolysis stage occurs. This step behaviour is overall endothermic.

Lastly, pyrolysis products undergo oxidation and reduction reactions that transform them into char, steam, tar and gases. Gasification (thermal stage) is characterized by temperatures between 800 to 1400°C, and final gas yield can rise up to 90 wt.%. The oxidation reactions are highly exothermic, causing a great increase in the temperature (up to 1100°C), thus, maintaining the endothermic stages. Supplementary fuels such as coal are however generally necessary to maintain the desired gasification temperatures in the reactor.

After the last stage, raw synthesis gas is reduced usually by water quenching. Other heat exchangers may provide further cooling, then particulate matter is removed via filtration or direct-water scrubbing. Gas cleaning systems are one of the most costly parts of gasification plants.

In fact, for most applications, the content of dust and tar in the gas must be removed. Tar, which is a complex mixture of condensable hydrocarbons, can condense problems in the engines and turbines in which the gas is burnt. Researchers are working on solutions for primary or downstream removal of tar from syngas. Primary methods focus on the use of catalysts also of natural origin.

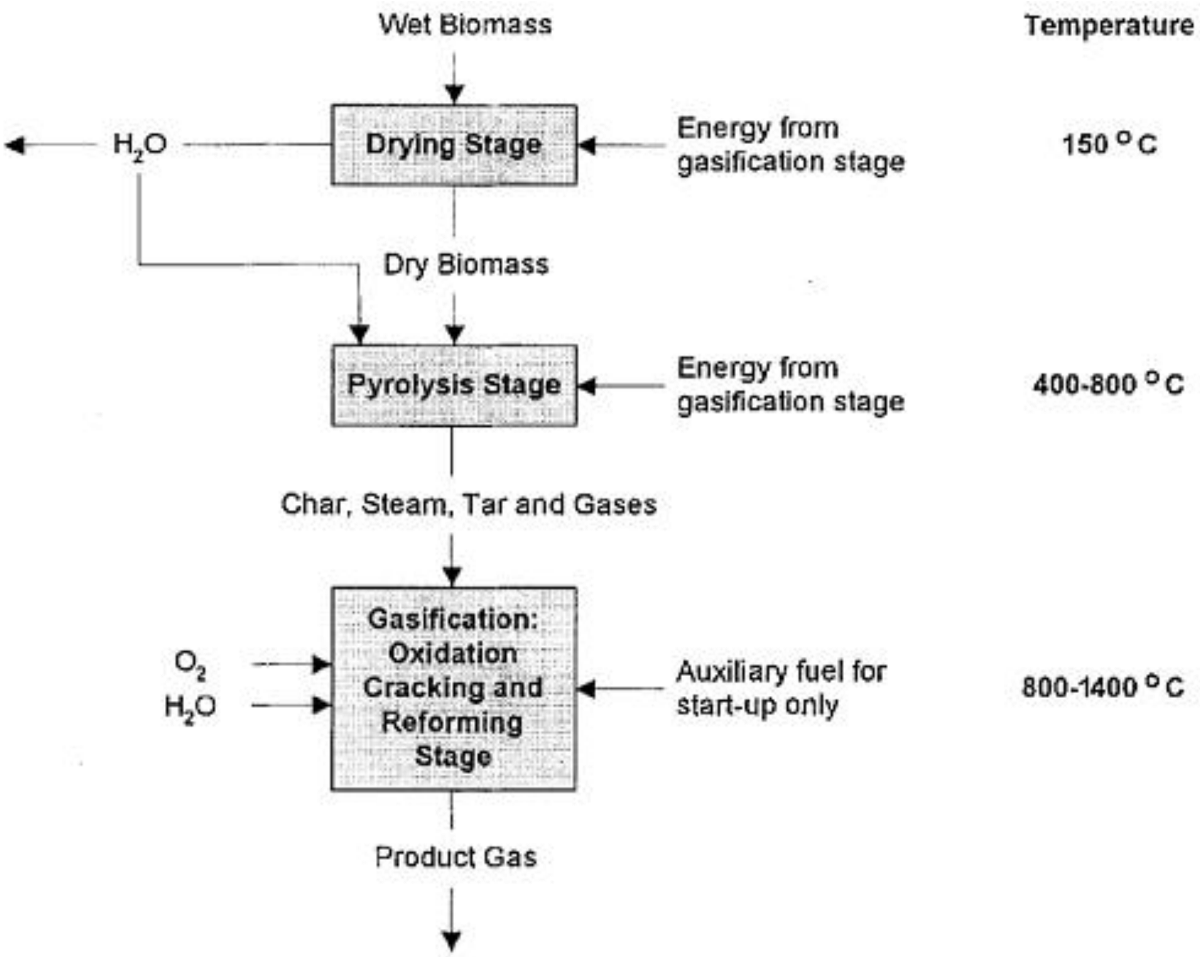


Figure 21

Conclusions

After an overview on sewage sludge characteristics and disposal possibilities, some general evaluations can be made. Sewage sludge coming from municipal wastewater treatment plants has a high water content. Dewatering is therefore the first challenge to face, in order to reduce sludge disposal volumes. Dewatered sludge has a good heating value, high content in soil nutrients and good soil stabilization properties. Anyway, due to the contextual high content in heavy metals, many of the disposal routes based on these good properties are difficult to develop. Incineration partially solves dewatering problems and reduces volumes to be disposed of, but does not offer a complete and sustainable solution.

It is now a fact that is important to investigate further, in order to discover novel trends in sewage sludge handling and to make the existing ones economically viable. Nevertheless, in order to reach a zero-landfill sludge management solution, it is necessary to define new criteria and parameters for sewage sludge collecting and disposal routes. A focus on industrial symbiosis could represent a first approach to this issue: a cross-sectorial approach could lead to exploitation of novel and alternative value chains with strong connections to waste hierarchy.

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