Observing the effects of digestion and chemical dosing on the calorific value of sewage sludge

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Abstract: New legislation being introduced in Europe for the removal of the macronutrients nitrogen and phosphorous is causing the fundamental composition of sludge to change. Nitrogen removal requires longer residence times during activated treatment, and phosphorous removal can involve the supplementation of chemicals such as ferric. In addition, there is increasing pressure to capture energy from sludge due to incentives which encourage renewable energy recovery. Energy from sludge may be recovered as biogas or as fuel which is combusted. However, little is known about the effects of legislative change on the energy value (calorific value) of the sludge. This paper describes the analysis of numerous samples of raw, digested and chemically treated sludge for chemical composition and calorific value and compares the results against theoretically derived results. A simple formula is proposed based on the findings, which can be used as a primary estimate for calorific value.

Keywords: Calorific value; digestion; Du Longe equation; energy recovery; ferric addition

INTRODUCTION

Over recent years, evolving legislation in Europe is leading to the installation of processes which fundamentally change the composition of sewage sludge. For example, the implementation of the Urban Waste Water Treatment Directive (UWWTD – 91/271/EEC) has led to a large number of activated sludge plants being upgraded to remove ammonia, and the use of various chemicals — principally ferric — for the removal of phosphorous in the form of phosphate salts (Forster, 2003; Barber, 2005). However, to date, little is understood about affects that ferric addition has on either the performance of downstream unit operations (such as sludge digesters), or the properties of the sludge itself. Whilst European Legislation and the Waste Hierarchy hold agricultural recycling of treated sludge to land as the preferred end use for sewage sludge, other drivers are influencing the long term security of this outlet. These revolve around two principal issues, firstly acceptance by both public and the farming community, and secondly the increasing importance given to the production of renewable energy. This has led UK Water Companies to assess the long-term risks associated with sludge outlets resulting in the development of strategies involving a number of carefully chosen options in order to gain maximum benefits for sustainable sludge reuse. One of these outlets is the incineration of sludge. Currently, there are ten purpose built sewage sludge incinerators in the UK and Northern Ireland (Hudson and Lowe, 2003) and there are plans to increase this capacity.

As energy prices increase and the use of fossil-fuels is discouraged due to global warming, new renewable sources of energy are being sought, especially for high energy consumers such as cement manufacturers. Sewage sludge can be anaerobically digested to produce a methane-rich biogas which can be converted to renewable energy via a CHP plant. Furthermore, sewage sludge has been successfully used as both wet-cake and as dried sludge pellets in coal-fired power stations in Europe (Werther and Ogada, 1999). The continued use of sludge in energy reuse outlets is critically dependent on understanding its thermal properties. Despite this, there is a paucity of information regarding these properties, and as previously mentioned, the composition of sludge is evolving necessitating the need for further work in these areas.
Calorific Value

The principal measurement of the energy in a substance is generally known as its calorific value (Lee and Huffmann, 2000). However, a number of various alternative nomenclatures can be found in the literature. The Gross Calorific Value (GCV also known as Higher Heating Value – HHV) is described as the enthalpy change or heat released when a chemical compound is stoichiometrically combusted and the products of combustion are cooled to the initial temperature (Lee and Huffmann, 2000). Here, stoichiometric combustion refers to complete combustion with no excess oxygen in the flue gas. The main units for GCV are kJ/kg, but it is also expressed in units of BTU/lb (where 1 kJ/kg = 0.43 BTU/lb). In contrast to the GCV, the Net Calorific Value (NCV also known as Lower Heating Value – LHV) is similar to the GCV except that the water produced from the combustion process is not condensed but retained as a vapour. Calorific values can also be expressed in terms of kJ/kg dry solids or kJ/kg LOI (Loss On Ignition). With sewage sludge, LOI is equivalent to the organic volatile solids fraction. From this point forward, calorific value will be referred to as Gross Calorific Value or GCV and will be expressed in terms of kJ/kg DS or kJ/kg LOI.

Gross Calorific value is experimentally measured using bomb calorimetry (British Standard 1016-105). With calorimetry, a known weight of material is ignited and burnt in an insulated vessel, which itself is contained inside a larger vessel containing water in contact with a thermometer. This apparatus is known as a bomb. Thermodynamic properties are calculated based on temperature change recorded. Bomb calorimeters are built to withstand large pressures changes. Electrical energy is used to light the material via a wire connected to the sample, and as the fuel is burning, it heats up the surrounding air, which expands and escapes through a tube in the vessel into the outer vessel containing the water. The temperature of the water allows for calculating calorie content of the fuel. Calorimeters are generally calibrated using a known mass of a highly pure reference standard which is generally benzoic acid.

Alternatively, gross calorific value may be determined theoretically from knowledge of its chemical composition using an empirically derived equation, generally known as the Du Long equation (Technical Report, CEN/TR 13767, 2004). The equation has been developed by many workers since its introduction and exists in many guises (mainly dependent on the units used). The following version is recommended as a first approximation for calculation of gross calorific value of sewage sludge (Technical Report, CEN/TR 13767, 2004):

\[
GCV = 32810C + 142246(H - O/8) + 9273S
\]  
--- (1)

Where: GCV units are in kJ/kg LOI; C, H, O and S are percentage compositions of carbon, hydrogen, oxygen and sulphur respectively. Equation (1) slightly overestimates the heat value of sludge with high organic nitrogen content due to: nitrogen association with hydrogen as an amine, and the production of nitrogen oxide during amine combustion reduces the heat released from hydrogen. Therefore the following equation has been recommended to calculate the GCV of sewage sludge:

\[
GCV = 32810C + 142246(H - O/8) + 9273S - [2189N(1-\mu) + 6489N\mu]
\]  
--- (2)

Where: N refers to the percentage fraction of nitrogen; \(\mu\) refers to the mass fraction of nitrogen which is converted to nitrogen oxide (generally in the range of 2 – 7%). Table 1 shows typical composition of various sludge types. Use of the data in Table 1 with equation 2 and assuming typical ash contents of 30% for primary, 20% for secondary 25% for mixed sludge, and 33.8% for digested (based on 45% destruction of 75% volatile solids content) and a figure of 5% for , the following theoretical values are obtained: Primary sludge = 17,810 kJ/kg dry solids (DS); Secondary sludge = 17,403 kJ/kg DS; Mixed sludge = 17,473 kJ/kg DS; and Digested sludge = 15,361 kJ/kg DS.
Table 1 Typical elemental analysis of various sludge (Taken from Technical Report, CEN/TR 13767, (2004))

<table>
<thead>
<tr>
<th>Elemental Analysis</th>
<th>Primary</th>
<th>Secondary</th>
<th>Mixed</th>
<th>Digested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>60.0</td>
<td>53.0</td>
<td>57.0</td>
<td>67.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>7.5</td>
<td>7.0</td>
<td>7.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>28.0</td>
<td>30.5</td>
<td>30.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.0</td>
<td>9.0</td>
<td>5.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

**United Utilities**

United Utilities owns and operates the electricity distribution, water and wastewater networks in North West England. The company manages over 700 water and wastewater treatment works, 32,000 electricity substations and around 120,000 kilometres of pipes, sewers and cables. It is a major service provider in the competitive industrial water and wastewater market and is responsible for the relationship with 3.1 million household and business customers. Based on recent records, United Utilities produces approximately 213,000 tonnes sludge per year. The vast majority (over 70%) of this sludge is digested and primarily recycled to land. The remaining sludge is raw and treated with lime prior to land application. A small fraction (12%) of the sludge is incinerated in a purpose-built plant in Widnes.

For the purpose of this study, sludge samples were taken from works contributing to United Utilities’ incineration plant. The incinerator is currently designed to burn approximately 32,000 tonnes dry solids of digested sludge per year and a project is undergoing to expand this capacity to approximately 75,000 tonnes dry solids per year. Numerous sites contribute digested sludge to the incinerator. The sludge is pumped to the central site as a liquid with a dry solids content of 2 – 4%. The sludge is then dewatered at the site. Approximately half of the cake at the central plant is incinerated and the remainder is recycled to agricultural land. United Utilities’ two largest digestion plants contribute to the incineration plant. To the West of the plant, sludge is pumped from Liverpool, whilst Manchester supplies sludge from the East of the plant. The sludge quantities and digestion performance of the two sites are shown in Table 2 based on site records:

Table 2 Sludge throughputs and performance of Liverpool and Manchester digestion plants

<table>
<thead>
<tr>
<th>Site</th>
<th>Throughput to digester (TDSA)*</th>
<th>Throughput from digester (TDSA)*</th>
<th>Volatile solids destruction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liverpool</td>
<td>23,074</td>
<td>18,878</td>
<td>37.8</td>
</tr>
<tr>
<td>Manchester</td>
<td>39,063</td>
<td>24,080</td>
<td>47.8</td>
</tr>
</tbody>
</table>

* TDSA = Tonnes dry solids per annum

Volatile solids destruction is lower at Liverpool than at Manchester and is also lower than expected from theory (Barber, 2004). Reduced volatile solids destruction due to ferric has been observed under laboratory conditions (Johnson et al., 2003) which showed a reduction in biogas production of 12%. Ferric is used at various stages in the treatment process at Liverpool, primarily to assist with settling. Approximately 5,200 m³ per year is dosed at concentrations up to 110 mg/l. The digestion plant at Manchester digests indigenous as well as imported sludge.

**METHODS**

As mentioned previously, samples were taken from both Manchester and Liverpool for analysis due to their size and importance. Although ferric is not used for nutrient removal at Liverpool, this sludge was analysed as the site had historical records for ferric addition to improve settlement. (It is proposed to analyse other sites in the future for the effects of ferric addition for nutrient removal on gross calorific value when the plants come on-line and sufficient data becomes available.) For comparison, sludge samples were also analysed for a variety of works which do not have digestion. At these sites, the sludge is mixed with lime to achieve the necessary legislative requirements for application to land. The raw samples were analysed prior to the addition of the lime admixture.
Samples for all sludge were analysed for the following determinants: total moisture percentage; dry and volatile solids percentage (based on AWWA Standard Methods); elemental analysis for carbon, hydrogen, nitrogen and sulphur (using a combination of liquid and gas chromatography as described in Arankalle – 2005); oxygen (calculated by difference); Gross Calorific Value (by bomb calorimetry). Net calorific value was calculated from measured GCV readings and hydrogen content.

RESULTS AND DISCUSSION

Sensitivity analysis

Gross calorific values for the various sludge samples were calculated from theory using equation 2. Prior to comparison of theoretical and measured data, a sensitivity analysis was conducted using typical parameters for mixed sewage sludge with an ash content of 25%. The composition of mixed sludge was taken from Technical Report CEN/TR 13767 (2004) and shown in Table 1. Using these figures a GCV of 17,473 kJ/kg DS is obtained. Figure 1 shows the influence of each parameter on the overall result obtained.

\[
\text{Gross Calorific Value (kJ/kg DS)} = \frac{\text{Experimental GCV} \times (\text{DS})}{100 - \text{Moisture} - \text{Volatile Solids}}
\]

To plot the graph, the composition of each element was increased by 5, 10 and 20%. The composition of the remaining components was then recalculated to accommodate the increase caused by the changed element. As expected, increasing carbon and hydrogen (at the expense of the other constituents) causes an increase in the theoretical GCV. Increasing oxygen and ash causes a decrease, whilst nitrogen and sulphur have negligible effect (due to their low initial concentrations). The components are ranked in the following order of influence (with most influential first): oxygen > carbon > hydrogen > ash >> nitrogen > sulphur.

Comparison between measured and theoretical values

Measured data from the bomb calorimeter was compared with theoretical values using equation 2 by inputting measured chemical compositions for the different sludge samples. For the theoretical results it was assumed that the dry solids had no influence (either positive or negative) on GCV. The results compared well and are presented in Figure 2.
The dashed line in Figure 2 is the Y=X line, i.e. if there was a perfect correlation between theoretical and measured results. A summary of measured and theoretical gross calorific values is given later in Table 4. A reasonable fit is observed, although at higher measured values, a discrepancy appears. The most likely reason for the discrepancy is error in the measured data. Theoretical data was generally slightly lower than measured data, on average (based on 160 samples) 580 kJ/kg DS lower. This may be due to sampling errors, or it implies that the assumption that the inert ash content had no influence on GCV is incorrect.

A correlation was also observed between measured GCV and ash content. This is demonstrated in Figure 3. Apart from several measured readings above 20,000 kJ/kg DS, the data match was comparable to that found between measured and theoretically calculated data using the Du Long equation.

**Prediction of Gross Calorific Values**

As previously mentioned, data calculated using the Du Long equation was slightly lower than those data which were measured. Therefore, the data were recalculated taking this factor into account. Data were also predicted based on sludge ash content using the straight line relationship shown in Figure 3. As with the Du Long predictions, predictions based on ash gave slightly lower figures, and therefore, these were also recalculated to accommodate the initial reductions. The results of all these predictions are summarised in Table 3.
Table 3 Measured versus theoretical Gross Calorific Values for sludge tested

<table>
<thead>
<tr>
<th>Sludge Type</th>
<th>Gross Calorific Value (kJ/kg DS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured by bomb calorimetry</td>
<td>15,064 +/- 3040*</td>
</tr>
<tr>
<td>Calculated by Du Long equation</td>
<td>14,493 +/- 3050*</td>
</tr>
<tr>
<td>Calculated by Du Long equation with factor</td>
<td>14,964 +/- 3140*</td>
</tr>
<tr>
<td>Calculated from ash content</td>
<td>14,523 +/- 2636*</td>
</tr>
<tr>
<td>Calculated from ash content with factor</td>
<td>14,953 +/- 2725*</td>
</tr>
</tbody>
</table>

* Average figure for all measurements based on 160 samples

Both the factored Du Long and ash equation gave good predictions based on data measured by bomb calorimetry. The good results obtained using ash content only, implied that the compositions of the different sludge (i.e. raw, or digested, or ferric dosed) were similar enough not to make a significant impact on gross calorific value. The factored Du Long equation is essentially equation 2 multiplied by a factor of 1/0.9676, and the factored equation based solely on ash content of the sludge is described by equation 3:

\[
GCV(kJ/kg) = \frac{1}{0.9713}(22,840 - 23,854A)
\]

Where \( A \) = percent ash content in sewage sludge expressed as a decimal. Use of equation 3 on the theoretical data based in Table 1 gives gross calorific values within +/- 9% when compared with figures calculated using the Du Long equation. Based on these findings, it can be concluded that equation 3 can be used as a first estimate for gross calorific value determination in absence of bomb calorimetry or chemical composition data. However, for formal plant design, it is still recommended to take measurements based on these techniques.

Effect of sludge type on Gross Calorific Value

The results shown in Figure 2 and Table 3 were sub-divided dependent on sludge type to investigate the effect of treatment type on gross calorific value. These results are shown in Table 4.

Table 4 Influence of sludge type on various parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>Raw (kJ/kg DS)</th>
<th>Digested all (kJ/kg DS)</th>
<th>Digested no ferric (kJ/kg DS)</th>
<th>Digested with ferric (kJ/kg DS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured GCV</td>
<td>17,150</td>
<td>11,300</td>
<td>12,670</td>
<td>9,540</td>
</tr>
<tr>
<td>Theoretical* GCV</td>
<td>+/- 2290</td>
<td>+/- 2070</td>
<td>+/- 830</td>
<td>+/- 2025</td>
</tr>
<tr>
<td>Carbon (% of VS)</td>
<td>53.0</td>
<td>49.1</td>
<td>50.5</td>
<td>47.0</td>
</tr>
<tr>
<td>Hydrogen (% of VS)</td>
<td>7.8</td>
<td>7.5</td>
<td>7.6</td>
<td>7.3</td>
</tr>
<tr>
<td>Oxygen (% of VS)</td>
<td>33.6</td>
<td>35.7</td>
<td>33.9</td>
<td>38.4</td>
</tr>
<tr>
<td>Nitrogen (% of VS)</td>
<td>4.6</td>
<td>5.8</td>
<td>6.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Sulphur (% of VS)</td>
<td>0.9</td>
<td>1.9</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ash (as % of Total Solids)</td>
<td>25.6</td>
<td>46.5</td>
<td>42.8</td>
<td>52.0</td>
</tr>
</tbody>
</table>

* Based on Du Long equation and measured chemical composition and ash content

Unfortunately, due to constraints in the sampling, only samples exiting the digesters were analysed thereby preventing a direct comparison to be made between columns 2 and 4 in Table 4. Nevertheless, sufficient data is available to indirectly calculate the effect of digestion on gross calorific value. If one assumes that the sludge entering the digestion plants has composition and GCV as Table 4 and undergoes 48% destruction in
volatile solids content, then the ash content drops from 42.8% to 33.6% and the equivalent raw GCV becomes 14,210 kJ/kg DS. This is an increase of only 16%. Use of the theoretical data suggested in Technical Report CEN/TR 13767 (2004), supports this figure with a calculated drop of <15% caused by digestion based on 48% volatile destruction. This implies that on an LOI basis, digested may have higher gross calorific value than raw sludge. This infers that the reason for it having lower GCV than raw sludge on a kg DS basis is because of higher ash content. However, this contradicts other data (Manual of Practice FD-19, 1992) which presents carbon contents of primary sludge in the range of 55 – 68%. An established formula for biomass is C:H:O:N (Rittmann and McCarty, 2001) which implies 53% carbon. Table 1 shows a higher carbon content for digested sludge compared with raw, and the sensitivity analysis described earlier in the paper shows that increasing carbon content has a large positive influence on gross calorific value. This is an interesting area for future research and also implies that the biomass formula of C:H:O:N may not be appropriate for digested biomass. Further work is proposed to measure chemical composition of the sludge entering the digestion plants from this study to enable a direct comparison.

It is also interesting to note the effect of digestion coupled to chemical dosing on gross calorific value. The data collected for Liverpool (digested with ferric) is lower than Manchester (data without ferric) even though the ferric addition makes the Liverpool sludge dewater better. Typically, Manchester sludge dewater between 25 – 27% dry solids, compared with 27 – 29% dry solids for Liverpool. On a superficial basis, it could easily be assumed that the Manchester sludge is less likely to be autothermic prior to incineration, but the high ash content of the Liverpool sludge makes it less suited for incineration even though it is drier after dewatering. Furthermore, the influence of ferric on digestability of Liverpool sludge makes it difficult to predict gross calorific value.

Whilst ferric is added at Liverpool to aid settlement, further work is required to investigate the effects of ferric addition for nutrient removal. This work will be conducted when plants which have been upgraded for nutrient removal are on-line and sufficient data available.

CONCLUSIONS
Changing legislation and drivers encouraging energy reuse are increasing the need to understand the thermal properties of sludge.

The use of the Du Long equation to calculate gross calorific value for sewage sludge compared relatively well with values obtained by bomb calorimetry.

A correlation existed between ash content in the sludge and measured gross calorific value. Use of the correlation yielded results which were within 9% of figures measured by bomb calorimetry. Therefore, it is potentially possible to use sludge ash content to derive an approximation of gross calorific value in absence of other data.

Measured gross calorific values based on sludge type were approximately: 17,200 kJ/kg DS; 12,700 kJ/kg DS and 9,600 kJ/kg DS for raw, digested and digested with ferric sludge respectively.

The effect of digestion on gross calorific value reduction is lower than expected based solely on destruction of volatile solids. This may be due to a change in chemical composition caused by digestion.

REFERENCES


