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Wet Oxidation Technology – A potential biosolids management alternative

1. ABSTRACT

As New Zealand's landfill space becomes increasingly limited, diverting waste from these landfills has become a focus via the Waste Minimisation Act 2008. This includes finding alternative management strategies for the large percentage of municipal biosolids currently being landfilled. A wet oxidation process for municipal biosolids was investigated as a potential technology to avoid these biosolids from going to landfill. In essence, this technology uses high pressure and temperature in the presence of an oxidising agent to deconstruct municipal biosolids. Simultaneously, this technology may be controlled in a manner that creates value-added by-products.

By applying this technology to municipal biosolids, a substantive mass reduction of more than 90 per cent was achieved. In addition, process conditions were chosen such that readily degradable carbon compounds, such as acetic acid, were formed. These compounds were found to be excellent supplements for the enhancement of activated sludge treatment systems.

Subsequently, Environmental Life Cycle Assessment (LCA) of the wet oxidation process was used to compare strengths and weaknesses of this technology with landfilling, particularly for energy consumption, global warming potential, eutrophication potential and photochemical ozone creation potential. The wet oxidation scenario displayed a significant positive impact on global warming and eutrophication compared to landfilling, but displayed a relatively high energy requirement.

Overall, this technology has potential for significant improvements in biosolids management. Current investigations into this technology aim to optimise mass and energy flows. These will be key to the successful implementation of this technology within New Zealand.

2. INTRODUCTION

2.1 BACKGROUND

In a world of increasing demand for sustainable waste management, drivers for reducing waste volumes to landfills have become important. Here in New Zealand, the Waste Minimisation Act 2008 was introduced to "encourage waste minimisation and decrease waste disposal in New Zealand". Under the Act, a $10 per tonne levy (excluding GST) on all waste disposed to public landfill was imposed from 1 July 2009. The levy has the capacity to increase to $40/tonne under existing legislation.

Organic solid wastes create some of the greatest concerns regarding landfill operation. Typically, organic solids wastes (which include about 10 per cent municipal biosolids) represent over 60 per cent of total waste volumes entering municipal landfills in New Zealand. These organic solid wastes have a number of disadvantages associated with their disposal. Their high moisture content makes transportation costs high, leachate generated from these wastes contributes to eutrophication in recipient waterways and large volumes of methane, a potent greenhouse gas, are generated under classic landfill conditions.

Despite increasing legislative and economic pressures, significant diversion from landfills remains a considerable challenge. Technologies for organic waste diversion from landfills are often only partially successful due to a range of factors, including:

- Challenging energy balances (e.g. incineration or drying)
- Lack of sufficient markets for diverted products (e.g. mulches, compost)
- Significant land areas required (e.g. land application, vermicomposting)
- Odour generation (e.g. windrow composting)
- Real or perceived presence of contaminants and pathogens that preclude substantial re-direction (e.g. land application, composting).

In partnership with the Rotorua District Council (RDC), wet oxidation technology was investigated as an alternative technology to address the need to reduce municipal biosolids going to landfills. Technology to deconstruct waste sludge through oxidation was first practised in the Zimpro process in the early 1960s (Weemaes and Verstraete 1998). The currently-investigated wet oxidation technology has the potential to reduce solids levels (Strong *et al.* 2011a) and solubilise organic compounds (Weemaes *et al.* 2000) in order to create valuable simple short-chained organic molecules that then could be converted in a range of end-products, such as bio-energy, bio-plastics or carbon sources for the enhancement of denitrification (Strong *et al.* 2011b).

The objective of this paper is to give an overview of the laboratory-scale performance of wet oxidation technology using municipal biosolids. The laboratory results were then used to undertake a life cycle assessment of this wet oxidation technology and compared with landfilling as an alternative disposal option.

3 MATERIALS AND METHODS

3.1 BIOSOLIDS CHARACTERISATION OF WET OXIDATION FEED

The municipal biosolids currently dispatched from the Rotorua District Council Wastewater Treatment Plant to landfill were characterised in order to gain a better understanding of the characteristics of the potential wet oxidation feedstock solids. The municipal biosolids were subjected to solid state ^{13}C-NMR and elemental analysis in order to establish approximate compositions of carbohydrate, protein, fatty acids, aromatic compounds and elements in the biosolids.

3.2 WET OXIDATION PROCESS

The wet oxidation process has as its primary goal the complete destruction of the input material to carbon dioxide, ash and water but under certain conditions this solids destruction may be combined with product or energy generation for downstream utilisation. This is achieved through the controlled oxidative conversion of complex solid organics into short chained biodegradable compounds such as acetic acid.

The wet oxidation is achieved under conditions of elevated temperature and pressure. It involves heating sludge under pressure for short periods of time in the presence of air, oxygen or oxidising agents (Figure 1).

The wet oxidation process allows for the direct treatment of wet organic material, such as the biosolids produced in a municipal wastewater plant and is amenable to treating wastes that are either too concentrated, toxic or recalcitrant for anaerobic digestion or aerobic biological treatment, or too dilute/wet for incineration.

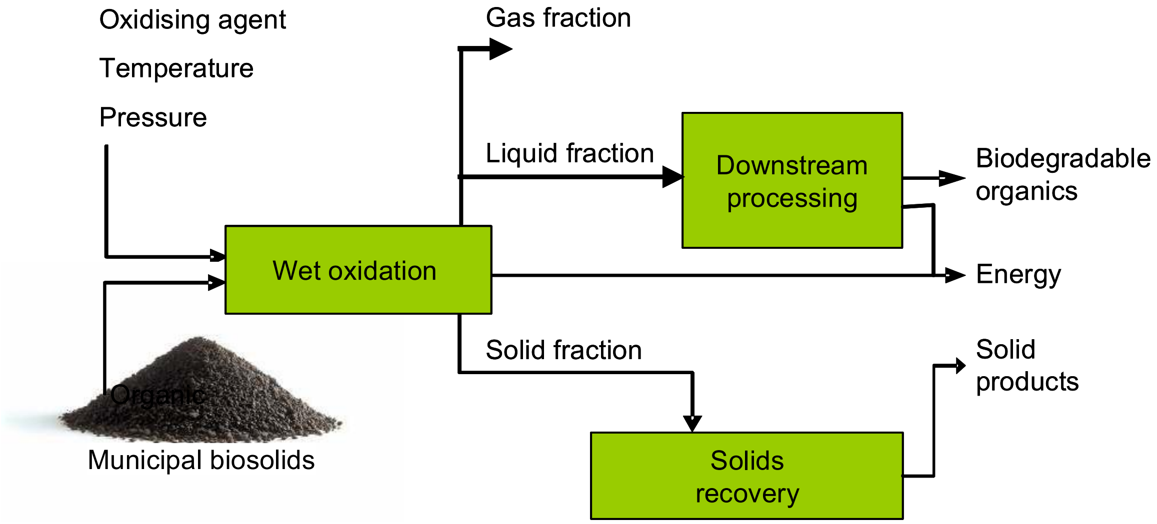

Figure 1: The concept of wet oxidation of municipal biosolids

3.3 PROCESS EVALUATION

3.3.1 Chemical

The municipal biosolids were subjected to laboratory-scale wet oxidation tests and the process conditions evaluated for solids destruction and creation of low molecular weight organic compounds. In particular, volatile fatty acids such as acetic acid, formic acid, ethanol, carbohydrates and metals were measured. In addition, a carbon mass balance for the oxidation process was determined.

3.3.2 Life Cycle Assessment

Environmental Life Cycle Assessment (LCA) was applied to the wet oxidation technology. LCA is an analytical tool for the systematic evaluation of the environmental impacts of a product system through all stages of its life. Our goal was to quantify the environmental impacts of treating biosolids from the RDC wastewater treatment plant using a wet oxidation process optimised for short chain organic compound production. This wet oxidation scenario was compared with a range of others scenarios to treat biosolids.

The first scenario was the currently used alternative: landfilling without methane capture. But because a recent survey estimated that in New Zealand on average approximately 50 per cent of methane from landfills is captured (MfE 2007), a second landfill scenario was compared whereby 50 per cent of methane emissions from a landfill were captured. These are the two most likely landfill scenarios in New Zealand. Lastly another wet oxidation process was assessed. This alternative wet oxidation scenario focussed more on energy than intermediates production.

In order to enable fair and relevant comparisons between the processes, the functional unit for comparisons was chosen as one tonne of biosolids from the RDC wastewater treatment plant with an assumed dry solids content of 15 per cent. The environmental impacts from the waste water treatment plant process and further upstream processing were excluded from the assessment of the environmental life cycle because these impacts were identical in all scenarios.

In addition, the impact from production start-up such as the production of buildings, excavation of landfills, processing equipment and vehicles was also included as it is recommended that capital goods be included in LCAs of waste management services (Frischknecht *et al*. 2007). The LCA analyses of the four technologies compared the impact that all upstream processes other than biosolids production (such as electricity and natural gas production, fuel use and production of oxygen) had on various environmental factors. The environmental factors (impact categories) chosen included energy consumption, global warming potential, eutrophication potential and photochemical ozone creation potential. These impact categories were chosen as they are amongst the most well-understood impact categories in LCA, and can be estimated with minimal site-specific data. A wider range of impact categories can be investigated in the future once site-specific data is available.

For the LCA modelling, the software tool and database GaBi 4.3 (GaBi 2010) was used. This encompassed various life cycle inventory databases including Ecoinvent database v2.0 (Frischknecht *et al.* 2005), a European database and New Zealand-specific electricity data. Models of the various treatment process scenarios were created and the different environmental impacts calculated. Environmental impacts calculated for the wet oxidation scenarios were based on the data measured in the laboratory-scale study described in this paper.

The environmental impacts calculated for the various scenarios relied partly on overseas data and partly on information from laboratory-scale experiments. It is therefore possible that environmental impact values presented here could differ to actual results when the various scenarios are undertaken in New Zealand at full scale. Nevertheless, the environmental impacts determined by the LCA modelling are useful to compare scenarios and highlight which environmental aspects should be a focus for improvement and which aspects were most advantageous for the various technologies.

4 RESULTS AND DISCUSSION

4.1 FEEDSTOCK CHARACTERISTICS

The biosolids feedstock used for the wet oxidation process consisted of approximately 32 per cent primary solids and 68 per cent waste activated sludge. This was a typical composition of biosolids generated by the RDC wastewater treatment plant.

Chemical characterisation of these biosolids showed that the most prevalent element was carbon followed by oxygen, hydrogen, and nitrogen (Figure 2A). Total heavy metals accounted for 0.08 per cent dry weight of the biosolids, and zinc and copper were the most prevalent heavy metals. In total, the measured elements accounted for about 97 per cent of the dry weight composition. The remainder may have been accounted for by “non-measured” elements, such as silicon, which is one of the most abundant elements in plants and soils. This element would be incorporated into the biosolids through food consumption and to some extent through the use of personal care products, defoamers, coatings and food additives.

Further characterisation of carbon, the most prevalent element in the biosolids, was undertaken to determine the biomolecular composition of these biosolids (Figure 2B). This was undertaken because the composition of the biosolids may have a direct impact on the formation of oxidation products.

Almost two thirds of the carbon content of the biosolids existed as protein and approximately a quarter existed as carbohydrate. Further inspection of the ^{13}C NMR spectra identified cellulose as the most predominantly carbohydrate. Cellulose is a major component of tissue paper and would have entered the waste stream through this route.

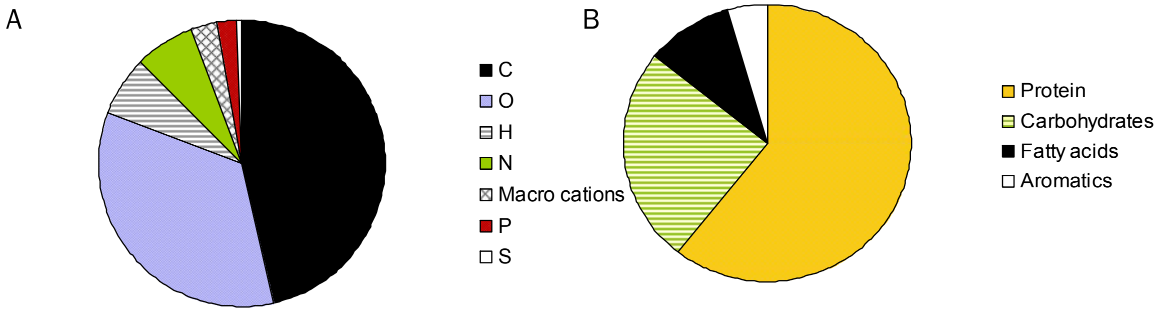

Figure 2. (A) Biosolids elemental composition (per centage dry solids) and (B) biosolids fatty acids, aromatics, carbohydrate and protein composition (per centage dry solids).

4.2 WET OXIDATION PROCESS

Wet oxidation was very successful in solids destruction. More than 90 per cent of the biosolids dry weight could be removed in a single stage. The remaining solids after the wet oxidation process were essentially a fine ash with low organic matter content (Figure 3).

Figure 3. Biosolids before and after wet oxidation.

These remaining solids had excellent dewatering characteristics compared to the original biosolids when measured by the capillary suction time (CST) test. Before wet oxidation, the biosolids measured an average CST of 19 seconds at a consistency of three per cent and 55 seconds at a consistency of six per cent. After wet oxidation, the remaining solids measured a CST of less than 1 second, indicating a much improved dewaterability.

Wet oxidation converted a large proportion of the solids carbon content to CO_2 gas or volatile organics. Less than one per cent of the original carbon content remained in the solid phase (Figure 4), confirming that the solids residue after wet oxidation was predominantly inorganic material. This highlighted that the process is performed under biologically sterilising conditions, creating sanitised products from the biosolids.

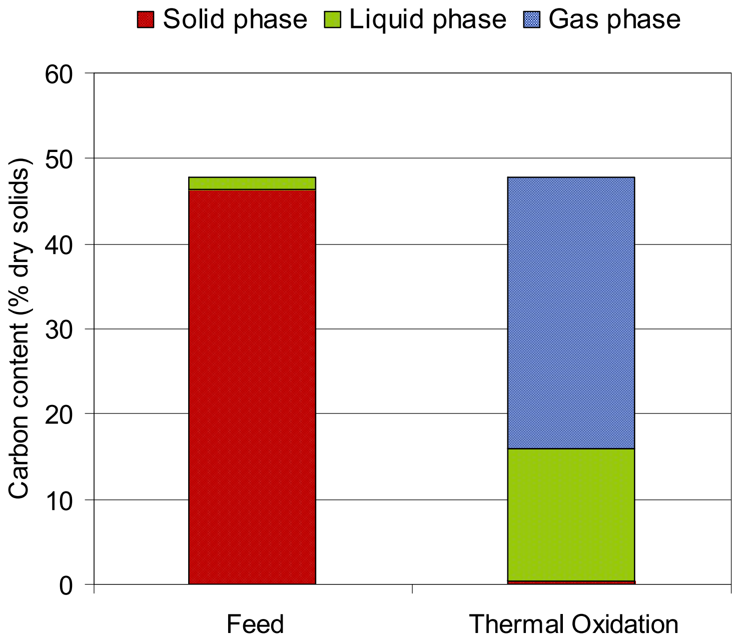

Figure 4. Fate of biosolids carbon after treatment.

A proportion of carbon from the biosolids was solubilised and converted to low molecular weight carbon compounds in the liquid phase. Approximately 30 per cent of the total carbon content was retained in the liquid phase during the wet oxidation process. The most abundant compound produced was acetic acid, which represented more than 35 per cent of the carbon in the liquid phase and was readily biodegradable.

Production of these biodegradable carbon products could be economically attractive. For example, for the RDC wastewater treatment plant at full scale, a wet oxidation process could potentially generate more than 500 kg acetic acid per day. This would be sufficient to substitute a significant proportion of ethanol that is dosed into the plant's biological nutrient removal (BNR) process to enhance denitrification.

4.3 HEAVY METALS AND THE WET OXIDATION PROCESS

During the wet oxidation process, heavy metals may have been solubilised. The degree of heavy metal solubilisation was determined from the presence of heavy metals in whole and filtered wet oxidation liquors (Table 1). Arsenic was the most soluble followed by copper and nickel. Other heavy metals were not very soluble and accumulated in the small fraction of inorganic solids generated by the wet oxidation process.

The concentrations of heavy metals that remained in the liquid fraction satisfied the EPA recommended limits for agricultural irrigation water for short term use (Rowe and Abdel-Magid 1995). And although recommended limits for long term irrigation of the filtered liquor would be exceeded for As (2.2 x), Cr (1.1x), Cu (14x) and Ni (4.5x), this liquor will be diluted by at factor greater than 1000x when reintroduced into the sewage treatment system to enhance denitrification.

At this dilution, the heavy metal levels would then also satisfy the World Health Organisation Water Quality Guidelines for Drinking Water (1993). Therefore heavy metals using the eco-indicator " micropollutants" have not been assessed in the following LCA assessment.

Table 1. Heavy metal levels in whole and filtered wet oxidation liquors and the degree of solubilisation for each of them.

Heavy metal	Whole liquor (g/m^3)	Filtered liquor (g/m^3)	Solubilised (per cent)
As	0.22	0.22	100%
Cd	0.0144	<0.0022	0%
Cr	1.16	0.11	9%
Cu	6.6	2.8	42%
Pb	0.42	0.0058	1%
Hg	<0.0042	<0.0042	-
Ni	2.2	0.9	41%
Zn	8.6	0.52	6%

4.4 LIFE CYCLE ASSESSMENT

Comparing the environmental assessment from the two wet oxidation technology scenarios (applied to RDC biosolids) with the two landfilling scenarios, one of which (landfilling without methane capture) is the currently used scenario, gave some insight into which environmental aspects could be improved and which aspects were most advantageous for the Rotorua case study (Figure 5).

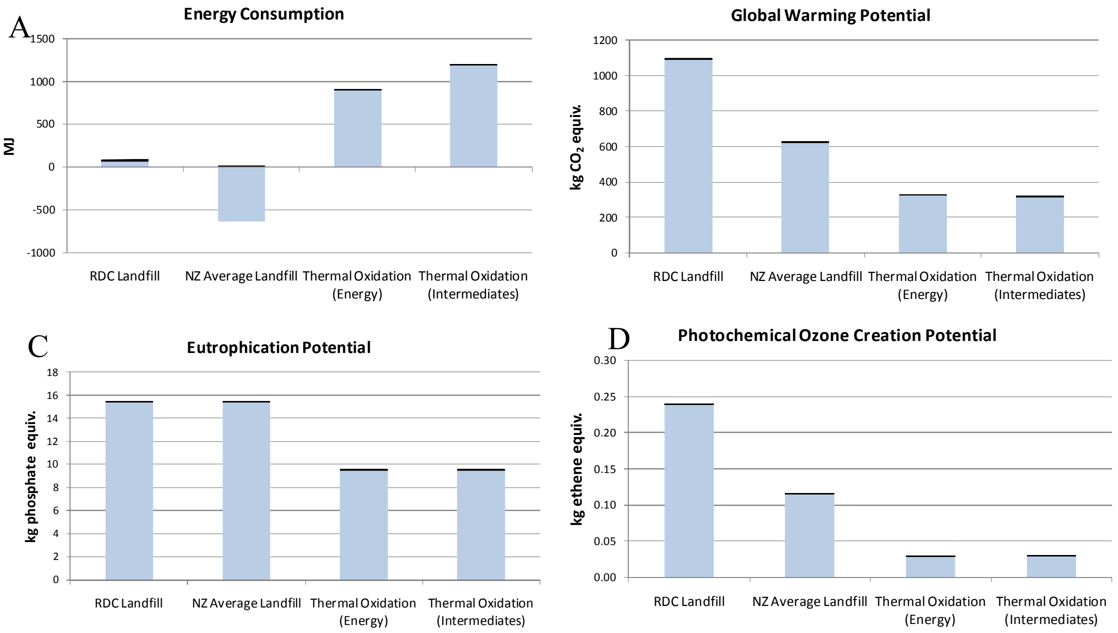

Figure 5. (A) Energy consumption, (B) global warming potential, (C) eutrophication potential and (D) ozone creation potential for various biosolids scenarios applied to RDC biosolids. The processing impact is shown in grey; capital goods are shown in black.

The scenario of landfilling of biosolids resulted in large methane emissions which could be more effectively used for electricity generation. This was clear from the New Zealand average landfill scenario with 50 per cent gas capture, which showed a negative energy consumption – Figure 5(A) when methane was captured. When such gases are not captured, they result in a high impact on the carbon footprint. Landfilling also resulted in a large photochemical ozone creation potential. Photochemical ozone or ground level ozone is readily formed in the atmosphere by the reaction of volatile organic compounds with nitrogen oxides in the presence of sunlight and heat, especially during hot summer weather. Furthermore, the landfilling scenario showed a relatively high eutrophication potential resulting from a high load of nitrogen and phosphorus compounds that could potentially leach from the landfill.

The wet oxidation scenarios displayed a greater positive impact on global warming, ozone creation potential and eutrophication – Figures 5 (B), 5 (C) and 5 (D). In contrast, these scenarios displayed relatively high energy requirements. This is due to the energy consumption of the process (high temperature and pressure) and also the requirement for oxygen, which has an energy-intensive production process. However, there is the potential for wet oxidation to be made self-sufficient, depending on the levels of biomass input and oxidative destruction. The, key to achieving this is improving the efficiency of oxygen input and oxidative conversion. The energy requirements of the wet oxidation process are being addressed in on-going programme investigations.

Production of capital goods such as the wet oxidation plant and the landfill facility contributed to less than one per cent of impacts in all scenarios, except for in energy consumption for the landfill scenarios. This percentage result is higher because the studied landfills have very low energy requirements in the use phase. It should be noted that the impacts of land use were not included in this assessment. This would give the wet oxidation scenarios credit for vastly reducing quantities of waste to landfill. Naturally, landfilling of biosolids would perform poorly in this category.

In summary, the wet oxidation process destroyed most of the solids content in the biosolids, which would result in very little material going to landfill. This would minimise transportation costs and impacts from methane in the landfill, whilst the produced biodegradable compounds could off-set dosing costs in wastewater treatment plants.

CONCLUSIONS

Central to success of wet oxidation process for the treatment of biosolids is the complete breakdown of the physical biosolids structure while retaining some solubilised readily degradable organic carbon compounds. This deconstruction process would lead to a substantive reduction in waste requiring landfilling.

Overall, the wet oxidation process was able to achieve:

- Substantive solids destruction and thus sludge volume reduction
- Oxidation of the refractory compounds to biodegradable products
- Improved sludge dewatering characteristics
- Creation of added value co-products
- Sanitisation of pathogens present within the waste.

These achievements indicated that this technology has a potential for future biosolids treatment provided that energy requirements for the wet oxidation process can be kept within acceptable limits. Future measurement and optimisation of the associated wet oxidation mass and energy balances, after completion of the wet oxidation pilot plant, will provide a better determination of the techno-economic efficacy of this wet oxidation technology. This would be of interest to potential end-users in the biosolids, municipal organic wastes and industrial organic waste management sector.

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