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Thermal characterisation of the products of wastewater sludge pyrolysis

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A B S T R A C T

The aim of this work was to characterise fundamental properties of the products of wastewater sludge pyrolysis and determine if the pyrolysis process of this material can be energy neutral. Wastewater sludge samples from different origin, including domestic, commercial and industrial sludges, were applied in the study. All samples were pyrolysed at a heating rate of 10 °C/min in a fixed bed reactor. The major gas species of pyrolysis, CO, CO_2, CH_4, C_2H_4, C_2H_6 and H_2, were monitored with gas chromatograph. Among the released species, hydrocarbons comprised half of the bio-gas fraction (50%) which suggests high potential for energy recovery through their combustion. Thermal properties of sludge samples were investigated using computer aided thermal analysis technique. The results showed that the energy required to pyrolyse wastewater sludge samples from room temperature to the carbonisation temperature of 550 °C varies according to the source and origin of the wastewater sludge and ranges from 1180 kJ/kg for the domestic to 730 kJ/kg and 708 kJ/kg for the commercial and industrial sludges, respectively. This study confirmed that in case of the commercial and industrial sludge samples, the recoverable calorific value from stoichiometric combustion of the pyrolysed bio-gas is sufficient enough to self-maintain the pyrolysis process. In case of the sample from domestic origin, the recoverable energy from combustion of the bio-gas compounds was lower than the energy required to heat the sample to the temperature of carbonisation. To pyrolyse this sample, excess energy will be required, possibly through combustion of the bio-oil fraction.

1. Introduction

Management of sewage sludge in an environmentally and economically acceptable way is an important challenge facing the society today. Due to industrialisation and urbanisation, production of wastewater sludge is increasing rapidly worldwide and this is expected to continue in the future. In the last few years the amount of wastewater sludge generation has increased dramatically [1,2]. For example the production of wastewater sludge in UK has reached nearly 1 million m^3/year, 50 million m^3/year in Germany and 4.2 million m^3/year in Switzerland, whereas in Singapore it is 170,000 m^3/year [3]. In Sydney alone the production of biosolids reaches 190,000 tones/year [4]. Consequently, disposal of wastewater sludge has become one of the main concerns for the modern society.

The most common methods for managing wastewater sludge disposal are landfilling, farmland applications and incineration but none of these methods are exempt from drawbacks [5]. Wastewater sludge can be applied to agricultural, forest or disturbed lands as fertiliser. However, presence of metals and trace elements in wastewater sludge limits their use in agricultural application as a fertiliser. Disposal of wastewater sludge through landfilling should be avoided as it subtracts the soil from agricultural use [6,7]. On the other hand incineration reduces the volume of the sludge but it is costly and generates emissions to air, soil and water [8].

New alternative disposal methods are currently being investigated which minimise the current drawbacks. Pyrolysis of wastewater sludge with gasification could be an alternative and viable option for environmentally acceptable way to manage sludge disposal. The products of pyrolysis are bio-gas (non-condensable), bio-oil (condensable volatiles) and carbonaceous bio-char residue. The produced bio-gas could be used as an alternative energy source [9–11] or to supply heat for driving the pyrolysis process. The oil can also be modified to an alternative energy source or it may be applied as raw material for petrochemical production [12]. The solid carbonaceous bio-char residue is rich in elemental carbon and nutrients. It has potential to be applied in to the soil for improving N fertiliser use efficiency [13] or can be used as an adsorbent [14].

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To be able to have viable wastewater sludge pyrolysis process, it is desirable the pyrolysis to be energy neutral, which means that the energy required to pyrolyse the material is supplied through combustion of the evolved bio-gas compounds. In this study we investigate the fundamental properties of the products of wastewater sludge pyrolysis of samples collected from three different sources of wastewater. The aim of this study is to determine if the pyrolysis process can be energy neutral. The work applies a comprehensive thermal evaluation of the raw samples and determination of the bio-gas and bio-oil products of pyrolysis. In addition, elemental and mineralogical analysis and species quantification of the composition of wastewater sludge are established.

2. Experimental

2.1. Wastewater sludge materials

Three different types of digested wastewater sludge samples were used in this study. All three samples (B, C and M) were collected from urban wastewater treatment plants. Samples B and C originated from commercial and domestic sources, respectively, whereas sludge M originated from industrial wastewater source. The main physical and chemical characteristics of the sludge samples used in this study are given in Table 1. Each wastewater sludge sample showed differences in the intrinsic properties. Sample C was found to contain the highest ash content, whereas sample B contained the highest volatile matter content. Volatile matter was found to range between 45.9% and 53.2%. The moisture content of air-dried wastewater sludge was found to range up to 11.1% which is in the similar range to the values determined by Dogru et al. [11] who found the moisture content in sewage sludge at 11.75%. The amount of fixed carbon (FC) was found to vary from low (0.5%), in case of the domestic sludge, to around 10% for the commercial sludge samples.

Table 2 shows the major and environmentally most important trace elements present in the wastewater sludge samples. Concentrations of some of the elements are significantly different among the samples. For example the commercial wastewater sludge sample (sample B) showed the highest concentrations of antimony, boron, selenium, copper, lead, zinc and zirconium. The sample which was from domestic origin (sample C) showed the lowest amount of all trace elements, whereas the industrial wastewater sample (sample M) showed significantly higher values of arsenic, barium, silver, cadmium, and nickel, comparing to the other two samples.

The mineralogical data of the three samples analysed by X-ray fluorescence (XRF) spectrometry based on the Australian Standard Method AS 1038.14.3 are displayed in Table 3. There are 15 minerals present in all three samples. Sample B was found to contain the highest silicon content, whereas sample C contained the largest concentration of iron oxide. Sample M contained large amount of silica and alumina. In case of samples C and M concentration of phosphorus pentoxide (P_2O_5), an important nutrient indicator, was significantly high.

Table 1
Proximate and ultimate analysis of wastewater sludge (wt%).

	Moisture %	FC %	VM %	Ash %	C %	H %	N %
B	5.6	10.3	53.2	30.9	35.2	5.62	3.79
C	11.1	0.5	45.9	42.5	23.5	3.61	3.06
M	7.6	8.2	50.2	34.0	32.3	4.47	3.45

FC = fixed carbon, VM = volatile matter.

Table 2
Trace element analysis of wastewater sludge (mg/kg).

	B	C	M
Arsenic	3.9	3.4	5.9
Boron	22	6	18
Antimony	5.1	2.5	4.7
Selenium	4.1	1.6	3.8
Silver	4.4	7.2	16
Cadmium	2.5	0.91	2.6
Barium	280	130	330
Beryllium	0.4	0.2	1
Cobalt	38	<2	430
Chromium	59	79	94
Copper	1400	370	660
Lanthanum	21	17	13
Manganese	120	480	150
Molybdenum	11	10	22
Nickel	28	34	54
Lead	190	35	85
Tin	67	36	130
Strontium	99	73	150
Vanadium	16	16	31
Yttrium	5	2	6
Zinc	1300	470	1200
Zirconium	110	43	85

2.2. Thermal analysis

The wastewater sludge samples collected from three different wastewater treatment plants were subjected to thermal evaluation to determine their behaviour during pyrolysis. Specific heats of the wastewater sludge samples were determined using an instrument based on the Computer Aided Thermal Analysis technique. Detailed description of the experimental procedure can be found elsewhere [15]. The thermal analysis apparatus consisted of an infrared furnace and arrangement of internals for heating of a packed bed of sample. Each analysed sample weighing between 2.1 g and 2.85 g was packed in a silica glass tube to the density of 870 (sample C) and 925 kg/m^3 (sample B) and 1080 (sample M). The packed sample was insulated on the sides with ceramics and heated under argon atmosphere with a graphite heating element positioned inside the furnace. The heating rate of the furnace was fixed at 10 °C/min and the heating was carried out until the graphite temperature reached 800 °C. Temperatures of the graphite, surface and centre of the packed sample were acquired at a frequency of 1 Hz using chromel–alumel thermocouples.

The specific heat was estimated simultaneously by applying an inverse numerical technique to the measured temperatures. For the purpose of calculations, the sample was divided into a grid with

Table 3
Mineralogical analysis of the wastewater sludges (% dry basis).

	B	C	M
SiO_2	65.0	10.2	44.0
Al_2O_3	8.6	4.7	11.7
Fe_2O_3	5.3	56.5	20.0
CaO	6.1	4.4	9.0
MgO	2.0	1.2	1.7
Na_2O	0.10	0.40	0.25
K_2O	0.89	0.31	0.84
TiO_2	1.1	0.50	0.86
Mn_3O_4	0.04	0.19	0.06
P_2O_5	5.6	22.0	9.1
SO_3	3.4	0.57	4.0
SrO	0.03	<0.01	0.04
BaO	0.08	0.01	0.10
ZnO	0.26	<0.01	0.11
V_2O_5	0.02	0.01	0.02