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Revisiting the elemental composition and the calorific value of the organic fraction of municipal solid wastes

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ABSTRACT

In this work, the elemental content (C, N, H, S, O), the organic matter content and the calorific value of various organic components that are commonly found in the municipal solid waste stream were measured. The objective of this work was to develop an empirical equation to describe the calorific value of the organic fraction of municipal solid waste as a function of its elemental composition. The MSW components were grouped into paper wastes, food wastes, yard wastes and plastics. Sample sizes ranged from 0.2 to 0.5 kg. In addition to the above individual components, commingled municipal solid wastes were sampled from a bio-drying facility located in Crete (sample sizes ranged from 8 to 15 kg) and were analyzed for the same parameters. Based on the results of this work, an improved empirical model was developed that revealed that carbon, hydrogen and oxygen were the only statistically significant predictors of calorific value. Total organic carbon was statistically similar to total carbon for most materials in this work. The carbon to organic matter ratio of 26 municipal solid waste substrates and of 18 organic composts varied from 0.40 to 0.99. An approximate chemical empirical formula calculated for the organic fraction of commingled municipal solid wastes was $C_{32}NH_{55}O_{16}$.

1. Introduction

The elemental (or ultimate) composition (i.e., commonly the content of C, N, H, S, O) and the calorific value (or energy content) of individual municipal solid waste (MSW) components can be usually found in Alter et al. (1974), Kaiser (1966) and Tchobanoglous et al. (1993). These values, although widely used, are partly based on original research that was performed more than 30 years ago. Therefore, an update was deemed necessary, since source materials, MSW composition and instrumental analysis techniques may have changed throughout the years. Such values are useful when it is to develop stoichiometric equations to calculate air requirements and gaseous byproducts during MSW incineration or develop MSW related biochemical equations. On the other hand, the elemental composition of commingled MSW has been often reported in the literature (Abu-Qudais and Abu-Qdais, 2000; Ikeguchi et al., 1994; Kathiravale et al., 2003; Liu et al., 1996). The elemental composition of MSW can significantly vary among countries, regions and cities, as a result of differences in the physical composition of MSW. The physical composition of MSW is usually dependent on the socio-economic conditions of a country, its population size, the climatic conditions and the national environmental legislation (Abu-Qudais and Abu-Qdais, 2000).

The knowledge of the calorific value of MSW is necessary when it is to design MSW incinerators for energy recovery purposes. When direct calorific value measurements are not feasible, empirical models can be useful to predict the calorific value of MSW (Liu et al., 1996). Several models have been developed to describe and predict the energy content of commingled MSW. The common independent variables in such empirical models are either the elemental composition (Liu et al., 1996), the physical composition (Abu-Qudais and Abu-Qdais, 2000; Khan and Abu-Gharara, 1991) or the proximate composition (i.e., the content in volatile matter, moisture, fixed carbon or ash) of MSW (Kathiravale et al., 2003).

Table 1 summarizes some of the published models that correlate the energy content of MSW with its elemental (ultimate) and proximate composition. According to models 1–10, carbon appears to be the dominant predictor of calorific value, except in model 2 (Chang model). Nitrogen and sulfur do not appear in all of the models, whilst hydrogen and oxygen are almost always present, except in model (5) in which hydrogen is absent. Oxygen is a common predictor of the calorific value with either a positive or a negative coefficient. Models 11–14 are empirical formulas that are based on the proximate analysis of MSW and include the organic matter content (i.e., volatile matter) as the main predictor of calorific value. The moisture content appears in some of the models that are based on the elemental composition as well as in models 13 and 14.

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Table 1
Empirical models to predict the calorific value of MSW as a function of its elemental and proximate composition.

Model name	Equation	Source
(1)	CV = 99.5·C − 136.2·H + 61.9·O + 143.1·N − 1392.6	Kathiravale et al. (2003)
(2) Chang model	CV = 8561.1 + 179.7·H − 63.9·S − 111.2·O − 91.1·Cl − 66.9·N	From Kathiravale et al. (2003)
(3) Wilson model	CV = 7831·Corg + 35.9(H − O/8) + 2212·S − 3545·Cinorg + 1187·O + 578·N	From Kathiravale et al. (2003)
(4) Mott and Spooner model	CV = 80.3·C + 338.9·H − 3.47·O + 22.49·S	From Kathiravale et al. (2003)
(5)	CV = 1558.8 + 19.96·C + 44.3·O − 671.8·S − 19.92·W	Liu et al. (1996)
(6) Modified Dulong model	CV = 80.5·C + 338.6·H − 42.3·O + 22.2·S + 5.55·N	From Tchobanoglous et al. (1993)
(7) Steuer's model	CV = 81·(C − 3·O/8) + 171·O/8 + 345·(H − O/16) + 25·S − 6·(9·H + W)	From Liu et al. (1996)
(8) Scheurer-Kestner's model	CV = 81 (C − 3·O/4) + 342.5·H + 22.5·S + 171·O/4 − 6·(9·H + W)	From Liu et al. (1996)
(9) Boie model	CV = 83.2·C + 274.3·H − 25.8·O + 15·N + 9.4·Cl + 65·P	Corbitt (1989)
(10) Vondracek model	CV = C. (89.17 − 0.0622·C1) + 270(H − O/10) + 25·S	Corbitt (1989)
(11)	CV = 85.1·OM − 1671.9	Kathiravale et al. (2003)
(12)	CV = 85.1·OM − 28.2·FC − 1337	Kathiravale et al. (2003)
(13) Traditional model	CV = 45·OM − 6·W	From Abu-Qudais and Abu-Qdais (2000)
(14) Bento's model	CV = 44.75·OM − 5.85·W + 21.2	From Abu-Qudais and Abu-Qdais (2000)

CV: calorific value expressed in kcal/dry kg in all equations; OM: organic matter (or volatile matter) in % on a dry weight (dw) basis; C: carbon (% dw); N: nitrogen (% dw); O: oxygen (% dw); H: hydrogen (% dw); S: sulphur (% dw); W: total moisture content (% dw); Corg: organic carbon (% dw); Cinorg: inorganic carbon (% dw); FC: fixed carbon (% dw); C1: carbon content (% organic matter basis); Cl: chlorine content (% dw); P: phosphorus content (% dw).

Researchers still seek a correlation between carbon content and the organic matter (or volatile solids) content. This would be desirable, since organic matter, which is commonly measured via a muffle furnace through a simple weight difference, is an easier analytical measurement compared to elemental carbon analysis. The latter usually requires more sophisticated and expensive equipment, such as an elemental analyzer. According to the formula included in Diaz et al. (1993), the organic carbon content of waste materials is 55.6% of the organic matter (volatile solids) content. Ikeguchi et al. (1994) produced an improved empirical formula in which the carbon content of MSW is a linear function of the volatile matter content as well as of the physical composition of MSW (i.e., the combined percentage of plastics, leather and rubber). The relationship between carbon content and organic matter content will be also investigated here.

Based on the above, the objectives of this work were to:

(1) Measure the elemental content (C, N, H, S, O) of 26 MSW organic components and develop approximate empirical chemical formulas for each individual component.
(2) Measure the calorific values of the aforementioned components and develop an empirical equation to describe calorific value as a function of the elemental composition. A comparison with similar empirical formulas was made.
(3) Investigate the relationship of organic matter content and total carbon (TC) content.

The results of this work can be useful when it is to theoretically calculate gaseous byproducts generated during the complete combustion of municipal solid wastes. In addition, the precise knowledge of the energy content of MSW is of key importance when evaluating the efficiency of municipal solid waste incineration.

2. Materials and methods

2.1. Material sampling

The MSW groups that were used in this research are included in Table 2. The constituents of these groups were all organic and were collected prior to their placement in a solid waste collection bin. In a similar older study (Alter et al., 1974), the individual materials had been separated directly from the solid wastes stream after disposal in waste bins placed in household curbs. This was not rendered necessary here, since most of the materials that were used in this work are expected to have the same structure after their disposal into waste bins.

Office paper and cardboard were collected from student housing and super-markets, while kitchen and toilet paper were purchased from local super-markets, as indicated in Table 2. The quantities of each paper component collected were between 1 and 2 kg. After random sampling, approximately 0.5 kg were selected from each paper component and placed for drying. Ground pork meat was purchased from a local butcher shop and some was grilled to provide the "cooked meat". Raw pasta was cooked to represent a typical "pasta waste". Raw fat was separated from raw pork stakes. Vegetables and fruit were purchased from a local grocery store and plastics were obtained from local super-markets. The amounts placed for drying ranged from 0.2 to 0.5 kg depending on the component, as shown in Table 2.

Commingled MSW were sampled from the inlet and outlet of an aerobic pretreatment (biodrying) facility in Heraklion-Crete (South Greece). The facility treats an average of 250 tpd of commingled MSW. MSW are first shredded via a shear shredder prior to their placement in the (bio)drying beds. After a 15-day drying period, MSW pass through a magnet to remove ferrous material and are then baled and landfilled. A negative aeration regime is maintained throughout the whole process. During eight sampling events in 2010 and 2011, four inlet and four outlet MSW samples were collected. The sampling at the inlet of the facility took place right after MSW shredding. A random MSW sample was received from the inlet bunker via a grab. Sampling at the outlet of the facility took place right after the removal of the ferrous metals. Between 8 and 15 kg (wet weight) were, then, manually selected from the above amounts at each location using a sequential quartering process and were shipped to the university laboratory in plastic buckets. Approximately 40–50% of the total wet amount received in the university was selected using the same quartering process, and was divided to five (5) sub-samples for moisture content determination.

2.2. Solids characterization and elemental analysis

The moisture content of each material was measured through weight difference at 75 °C till constant weight (USDA and USCC, 2002). The dried material was then ground using a solid waste cutting mill (RETSCH®, Model SM 100, Germany), equipped with a 1.5 mm mesh screen, and was homogenized for elemental analysis and calorific value quantification.

In the case of the commingled MSW that were obtained from the biodrying facility in Crete, the inorganic components present in the sample (stones, metals, glass, etc.) were manually removed after drying and prior to grinding. Therefore, only the organic