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Application of various statistical methods to evaluate thermo-analytical data of mechanically–biologically treated municipal solid waste

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ABSTRACT

Resource recovery and stabilization of waste organic matter before landfilling are crucial issues in waste management. These requirements are closely related to efficient separation of recyclables and well operated biological processes. Adequate analytical methods are a prerequisite to verify the realization of these purposes. A large data pool of mechanically–biologically treated (MBT) municipal solid waste originating from different Austrian treatment plants was investigated using simultaneous thermal analysis that comprises thermogravimetry/mass spectrometry (TG/MS) and differential scanning calorimetry (DSC). Biodegradation of MBT-waste is paralleled by decreasing enthalpies. Referring to organic matter enthalpy increases with progressing stabilization. Evaluation of thermal data was supported by multivariate data analysis. The efficiency of the biological pretreatment of municipal solid waste (MSW) compared to untreated MSW in landfills was verified by principal component analysis (PCA) of heat flow (DSC) profiles. Divergent input materials were identified by means of heat flow profiles and discriminant analysis (PLS-DA). Prediction models for the calorific value and the TOC (total organic carbon) based on DSC-profiles and partial least squares regression (PLS-R) resulted in a good correlation ($R^2 = 0.94$ in both cases). The root mean square errors of crossvalidation were 413 J g^{-1} and 1.5% referring to dry matter, respectively. Respiration activity (RA_4) was reflected by thermal analyses. The correlation was based on mass spectra of volatile combustion products and DSC-profiles. The correlation resulted in a coefficient of determination (R^2) of 0.87 and 0.82 respectively. Thermal analysis in association with multivariate statistical methods has proven to be a reliable method to verify efficient separation of the plastic fraction, stabilization by biological treatment and waste material composition.

1. Introduction

The European concept of a multi-barrier system for safe waste disposal has led to corresponding regulations in Austria. The Austrian Landfill Ordinance [1] requires the thermal or mechanical biological pretreatment of municipal solid waste (MSW) before landfilling that takes place after an as efficient as possible separation of the recyclable fractions resulting in “residual waste (resMSW)”. With several exceptions the pretreatment has been realized since 2004. In Austria 692,000 tons a year of municipal solid waste are processed by mechanical biological treatment (MBT). The mechanical step aims at separation of the materials that interfere with the biological process and at recovery of recyclables including the light plastic fraction for thermal use. The biological process effects stabilization of organic matter by microbiological degradation which results in mineralization [2], enrichment of hardly degradable substances and humification [2] to a certain extent. Mineral compounds contribute considerably to the stabilizing effect [3,4]. Stabilization of organic matter before landfilling reduces greenhouse gas emissions and metabolic products in the leachate significantly. The efficient separation of the high caloric fraction (plastics) and the sufficient stabilization are verified by the compliance with limit values according to the Austrian Landfill Ordinance [1]. For the first purpose the calorific value was limited to 6600 kJ kg^{-1} referring to dry matter. It is usually measured by the bomb calorimeter [5]. Stability is verified by biological tests in waste management practice. Respiration activity (RA_4) reveals the oxygen uptake by microorganisms over a 4-day-period. The gas generation sum over a 21-day-period (GS_{21}) indicates the gas forming potential under anaerobic conditions [6].

New analytical approaches for waste characterization and description of the behavior are research topics. Enzyme activities during olive mill waste composting were determined by Cayuela et al. [7]. Quantification of enzymatic activity was reported by Bastida et al. [8] who evaluated the long-term effect of the organic fraction of municipal solid waste on a semiarid degraded soil in Spain.

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Table 1
Sample ID, sample number, origin and input materials.

Sample ID	Number of samples	Origin	Input materials
MBT-total	330	17 Austrian MBT plants	resMSW/resMSW + SSL/resMSW + SSL + BIO
MBT-on	301 out of 330	MBT-materials from different plants of ongoing processes	resMSW/resMSW + SSL/resMSW + SSL + BIO
MBT-lf	29 out of 330	Stabilized MBT-materials intended for landfilling from 17 MBT plants	resMSW/resMSW + SSL/resMSW + SSL + BIO
MBT-C	18 out of 330	Austrian MBT plant C	resMSW
MBT-D	25 out of 330	Austrian MBT plant D	resMSW
MBT-J	16 out of 330	Austrian MBT plant J	resMSW
MBT-M	30 out of 330	Austrian MBT plant M	resMSW + SSL + BIO
MBT-O	22 out of 330	Austrian MBT plant O	resMSW
MBT-R	12 out of 330	Austrian MBT plant R	resMSW
oLF	58	Old reactor landfills from the 70s	MSW + construction waste
rLF	20	Recent reactor landfill (2004–2007)	resMSW without mechanical biological treatment
SSL	1	Austrian water treatment plant	Sewage sludge

MSW = municipal solid waste without any separation of recyclables and pretreatment, resMSW = residual municipal solid waste after partial separation of recyclables, SSL = sewage sludge, BIO = biogenic waste.

Apart from a variety of spectroscopic methods [9–14] simultaneous thermal analysis has proven to be appropriate for process control and stability determination of waste organic matter. The efficiency of leachate recirculation was investigated by Franke et al. [15] using pyrolysis/GC in association with mass spectrometry. These techniques were also applied by Dignac et al. [16] and Gonzales-Vila et al. [17]. Investigations of organic matter evolution in compost focused on pyrolysis FI-MS [18]. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were found to be reliable methods for monitoring aerobic biological processes in waste technologies [19–22]. Stabilization of sludge from wastewater treatment was characterized by Otero et al. [23] using TG. Multivariate data analysis is an indispensable tool for the evaluation of large data pools generated by such methods [24,25]. Thermal decomposition steps of a co-polymer were determined using Pyrolysis/GC–MS and TG/MS data and principal component analysis [26]. Conventional and spectral data of different waste materials (municipal solid waste, compost, landfills) have been evaluated by means of several multivariate statistical methods. Differentiation of compost classes was supported by thermogravimetric investigations [27]. Principal component analysis has been applied to reveal the inherent data structure [28–32], partial least squares regression for parameter prediction [33–39] and soft independent modeling of class analogy (SIMCA) for waste classification [33,40].

Simultaneous thermal analysis provides comprehensive information on complex waste materials due to the high number of generated data points that reveal physical and chemical properties that are related to the biological behavior. The application of multivariate statistical methods supports the detection of inherent features and the evaluation of the data pool according to different aspects. The aim of this study was to characterize a large sample set of MBT-waste originating from Austrian MBT plants by thermal analysis, biological tests and conventional parameters such as loss on ignition and total organic carbon (TOC), and to demonstrate several approaches of data evaluation. Relevant questions in waste management focus on the compliance with limit value in terms of material stability for safe disposal and on waste composition to adapt process operation in practice. Principal component analysis (PCA), discriminant analysis (PLS-DA) and partial least squares regression (PLS-R) were applied for process monitoring and evaluation, control of input materials and parameter prediction.

2. Materials and methods

Sampling took place according to OENORM S 2123-1 [41]. Sample ID (MBT-X = individual plant indicated by a capital letter), sample numbers, origin and input materials are compiled in Table 1. Seventeen Austrian MBT plants were represented by different numbers of samples. Depending on process operation different stages of degradation (weeks of treatment) were available. In total 330 MBT-samples were collected. “MBT-on” comprises 301 samples from ongoing processes from all 17 MBT plants. “MBT-lf” represents the stabilized MBT-materials intended for landfilling from all 17 MBT plants including 29 samples. Samples from 5 MBT plants (MBT-C, MBT-D, MBT-J, MBT-M, MBT-O) were used for specific data evaluation and highlighted in Table 1. These 5 plants provide 111 samples in total. The other 12 MBT plants provide 219 samples. For comparison reasons old landfills (oLF), a recent reactor landfill (rLF) and anaerobically stabilized sewage sludge from a waste water treatment plant were included.

2.1. Sample preparation

Fresh MBT-materials were shredded <20 mm. For the determination of respiration activity (RA_4) the fresh sample with a particle size of <20 mm was used. For chemical and thermal analyses the material was dried at 105 °C and milled by a multi-stage procedure to obtain a particle size of 0.25 mm for reproducible results as described by Smidt et al. [42].

2.2. Chemical and biological investigations

The loss on ignition (LOI) was determined by combustion at 550 °C in a muffle furnace. Total carbon (TC) and total inorganic carbon (TIC) were quantified by combustion in a CNS analyzer (vario MAX CNS, Elementar Analysensysteme GmbH, Hanau, Germany). Total organic carbon (TOC) was calculated by subtraction of TIC from TC. Respiration activity (RA_4) was investigated according to OENORM S 2027-1 [43]. For respiration activity the oxygen uptake is recorded for 4 days and referred to 1 g dry matter (DM). Reference analyses of the calorific value were carried out for 150 samples according to DIN 51900-1 [5] with the bomb calorimeter. The samples were randomly selected and covered the whole range of reactivity.

2.3. Simultaneous thermal analysis

Thermal analyses (thermogravimetry/mass spectrometry, TG/MS and differential scanning calorimetry, DSC) were performed under oxidative conditions using the instrument for simultaneous thermal analysis STA 409 CD Skimmer (Netzsch GmbH) with a coupled mass spectrometer (QMG 422). The heating rate was 10 K min^{-1} and the gas flow was set to 120 ml min^{-1}

(80% He/20% O_2). Weekly temperature and heat calibration were carried out by means of melting temperature of indium and zinc. An extended monthly calibration using the calibration set (Netzsch Calibration set for DTA/DSC) comprises 6 relevant metals for the temperature range from 30 to 1000 °C. A sample amount of 16.00 mg of MBT-material was combusted in an Al_2O_3 pan. Heat flow (DSC) profiles of the samples were corrected by subtraction of the DSC-profile of the empty pan from the sample curve. For data editing the integrated software (Proteus for TG and DSC, Quadstar 32-bit for MS) was used. Enthalpies were calculated by integration of the area below the DSC-curve and a horizontal baseline from 30 to 650 °C. Enthalpy was referred to dry matter (DM) and organic dry matter (ODM). In this case ODM derived from mass losses (TG) between 30 and 650 °C. Additionally enthalpies of the 1st exothermic reaction E1 (30–400 °C) and the 2nd exothermic reaction E2 (400–650 °C) were calculated separately. The two main exothermic reactions that roughly represent two fractions of MSW organic matter are separated by a minimum at 400 °C.

Mass spectra of volatile combustion products were recorded in the range of m/z 12–100. The ion current of masses that could be assigned to O_2 (gas flow) and water (m/z 16–18, 32) due to the order of magnitude was not included in data evaluation. Ion current intensities were weighed for multivariate data analysis. All investigations were carried out in duplicate.

2.4. Statistical and multivariate data analysis

A one-way ANOVA was performed using R-projects for Windows® (http://www.r-project.org/). Furthermore a post hoc-test which produces multiple comparisons between means of a factor was carried out. A Dunnett–Tukey–Kramer test was performed due to unequal size of sample sets [44]. Multivariate data analysis was carried out by means of the Bruker OPUS 5 Quant2® software package for prediction of the calorific value and the TOC by partial least squares regression (PLS-R) and DSC-data. The software Unscrambler 9.2 (Camo) was applied for prediction of respiration activity by PLS-R and MS-/DSC-data, and for principal component analysis (PCA) and discriminant analysis (PLS-DA) based on DSC-data. For the PCA the whole temperature range (30–950 °C), for PLS-R and PLS-DA the temperature range from 30 to 650 °C was used. By means of the PCA the complex information of the original variable set is reduced to a smaller number of latent variables (principal components) that explain as much as possible of the variance in descending order. This procedure reveals the underlying structure of data and contributes to data interpretation in that similarities and differences of sample characteristics are clearly presented. PLS-DA is a classification method based on partial least squares regression. The separation of two classes requires a response variable (+1 and −1) that codes for each membership class. Regressions between thermal data (DSC and mass spectra of combustion products) and the calibration components (calorific value, TOC, respiration activity) for parameter prediction were carried out by means of PLS-R and full crossvalidation. The prediction model is characterized by the coefficient of correlation (R^2), the root mean square error of crossvalidation (RMSECV), the bias and the ratio of standard deviation to standard error of performance (RPD) [45,46].

Table 2
Ranges of RA_4 (mg O_2 g^{-1} DM), LOI (% DM) and TOC (% DM) in MBT-samples from the ongoing process (MBT-on) and from the materials intended for landfilling (MBT-lf).

	RA_4 mg O_2 g^{-1} DM	LOI % DM	TOC % DM
MBT-on	1.1–85.5	19.6–89.1	9.4–50.9
MBT-lf	0.6–15.2	15.4–38.3	7.5–25.1

3. Results and discussion

3.1. Characterization by conventional parameters (LOI, TOC, RA_4) and DSC-profiles

The ranges of the LOI (% DM), TOC (% DM) and RA_4 (mg O_2 g^{-1} DM) in 330 MBT-samples are presented in Table 2. MBT-samples from the ongoing process (MBT-on) including input materials, and stabilized MBT (MBT-lf) are presented separately. The considerable decrease of all values in materials intended for final disposal (MBT-lf) is shown in Table 2 and demonstrates the efficiency of the biological treatment.

Mass losses during combustion of MBT-materials are recorded by thermogravimetry (not shown). Due to the release of organic matter by progressing mineralization, mass losses of organic matter abate, which corresponds to the trend of LOI and TOC. Biological degradation of MBT-waste is paralleled by decreasing heat flows and enthalpies respectively, and visualized by the DSC-profiles. Fig. 1 illustrates different stages of degradation: MBT-input (MBT-D-in/MBT-M-in), MBT-material treated for 33/20 weeks (MBT-D-33 w/MBT-M-20 w), stabilized MBT-material intended for landfilling (MBT-D-lf/MBT-M-lf) of a typical MBT-material (MBT-D, Fig. 1(a)) and a special MBT-waste containing the biogenic fraction and sewage sludge (MBT-M, Fig. 1(b)). Typical MBT-materials comprise only residual municipal solid waste (resMSW). It is obvious that waste composition and degradation shape the heat flow profile. The content (∼30%) of sewage sludge in MBT-M is reflected

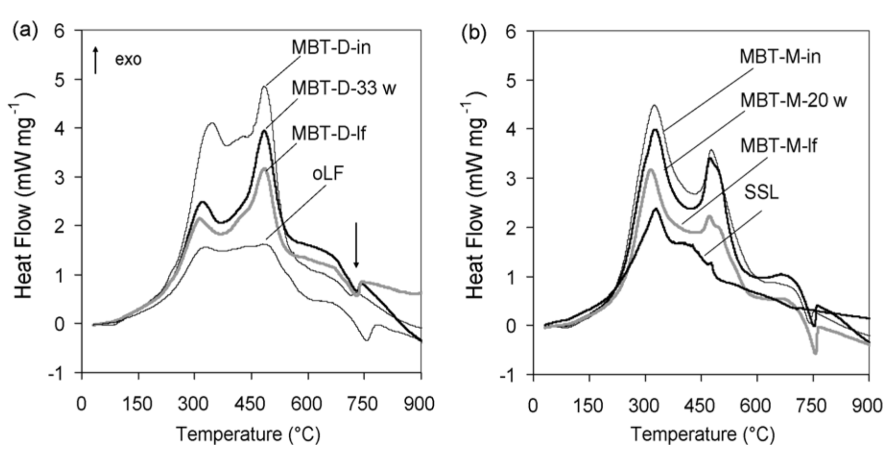

Fig. 1. (a) Changing heat flow profiles during the biological treatment of a typical MBT-waste (MBT-D) and (b) of a MBT-waste with a special composition (MBT-M); additionally (a) heat flow profiles of an old landfill (oLF) and (b) sewage sludge (SSL, scaled down by factor 0.5).

Table 3
Enthalpies based on DSC-curves (30–650 °C) of MBT-D presented in Fig. 1(a), referring to dry matter (DM) and organic dry matter (ODM).

Sample ID	Enthalpy J g^{-1} (DM)	Enthalpy J g^{-1} (ODM)	ODM (%)
MBT-D-in	7383 ± 250	12,701 ± 642	58.1 ± 0.3
MBT-D-33 w	5829 ± 157	21,196 ± 571	27.5 ± 0.4
MBT-D-lf	4779 ± 123	33,257 ± 855	14.4 ± 0.2
oLF	3267 ± 148	22,392 ± 1017	14.6 ± 0.1

by a prominent first exothermic peak as shown by the DSC-profile of pure sewage sludge (SSL). The decay of calcium carbonate is indicated by the endothermic reaction >650 °C (arrows). For comparison reasons the heat flow profiles of an old landfill (oLF) from the seventies and of sewage sludge from a waste water treatment plant are presented in Fig. 1(a) and (b) respectively. The two distinct exothermic peaks of organic matter fractions decrease with age (oLF). Stabilization leads to decreasing peak intensities and a shift of exothermic reactions towards higher temperatures.

Table 3 compiles the data of enthalpies based on the DSC-curve (Fig. 1(a)). Enthalpies are referring to dry matter (DM) and organic dry matter (ODM). The enthalpy of the whole waste sample referred to DM decreases with progressing degradation. By contrast, enthalpies referring to ODM display a considerable increase during the degradation process that can be ascribed to changing chemical and physical properties of stabilized organic matter [20]. Besides mineralization synthesis of stable organic molecules (humic substances) takes place during degradation. Although humification is not the dominant process in resMSW [2] it can play a role to a certain extent, especially if biogenic materials are not separated [47]. The enthalpy of the remaining organic matter does not necessarily increase, if the responsible chemical changes do not take place or only to a small extent due to the high content of mineral compounds. This effect is revealed by the old landfill (oLf) where construction waste was mixed with municipal solid waste. The relation between waste organic matter stabilization, especially the mechanisms involved, and the development of enthalpies need systematic investigation at a molecular level.

A more detailed insight is provided by the separate calculation of enthalpies below the 1st exothermic peak (E1) in the temperature range from 30 to 400 °C and below the 2nd exothermic peak (E2) in the range from 400 to 650 °C (Fig. 2). Fig. 2(a) and (c) displays the range of enthalpies (330 MBT-samples, 58 oLf-samples, 20 rLf-samples) referring to DM 2(a) and ODM 2(c). Fig. 2(b) and (d) illustrates the development of enthalpies in the ranges 30–400 °C (gray bar) and 400–650 °C (shaded bar) of a typical MBT-material (MBT-D). Enthalpies are referring to DM (Fig. 2(b)) and ODM (Fig. 2(d)). The enthalpy of the 2nd organic matter fraction exceeds the enthalpy of the 1st fraction. The comparison of mean values calculated by ANOVA resulted in a significant difference between the mentioned groups in Fig. 2 (p-value = 0.000) at a 95% significance level. The calculated power of the ANOVA is 1 and reflects the high significance of the test. The power ranges between 0 and 1, with 1 being the best [48]. Due to the results of ANOVA a post hoc-test called Dunnett–Tukey–Kramer test was performed to demonstrate the difference and the grouping of sample sets. The results are summarized in Table 4. The data obtained reflect the similarity of E1 (DM/ODM) and E2 (DM/ODM) of MBT-waste

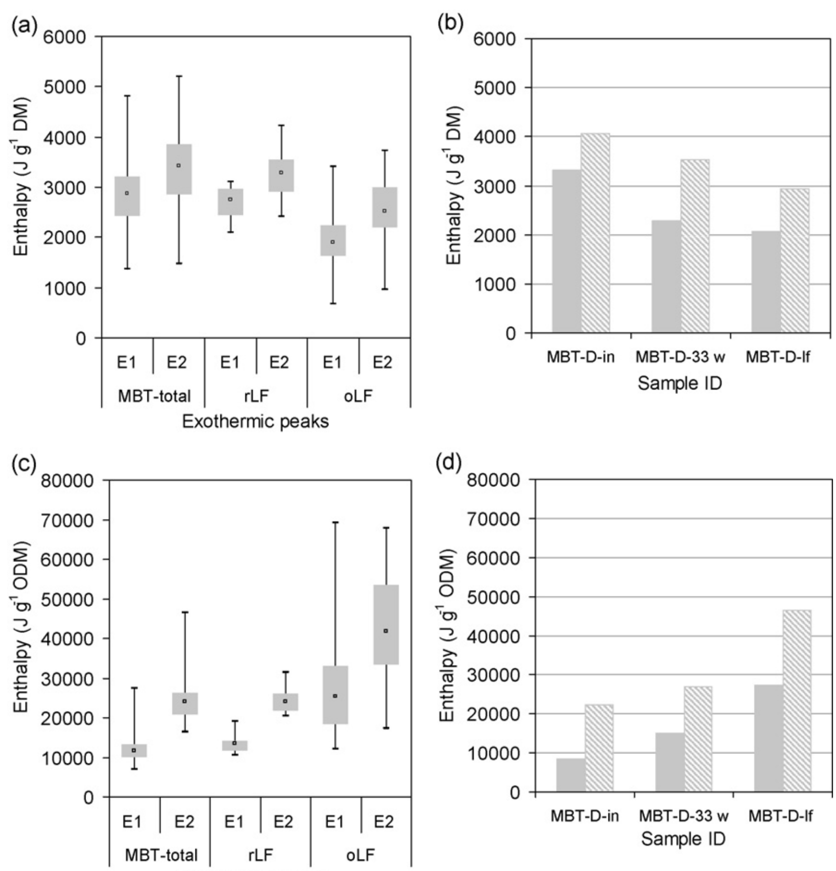

Fig. 2. (a)–(d) Median, minima, maxima and 25% and 75% quantile of calculated enthalpies for the 1st (E1) and 2nd (E2) exothermic reaction in 330 MBT-samples (MBT-total), 20 recent reactor landfills (rLF) and 58 old reactor landfills (oLF), referring to DM (a) and ODM (c); development of enthalpies (E1 and E2) referring to DM (b) and ODM (d) during the biological treatment of a typical MBT-waste (MBT-D).

Table 4
Results of Dunnett–Tukey–Kramer test DM/ODM.

	MBT-total-E1	MBT-total-E2	rLF-E1	rLF-E2	oLF-E1	oLF-E2
MBT-total-E1	–					
MBT-total-E2	1/1	–				
rLF-E1	0/0	1/1	–			
rLF-E2	1/1	0/0	1/1	–		
oLF-E1	1/1	1/0	1/1	1/0	–	
oLF-E2	0/1	1/1	0/1	1/1	1/1	–

0 = no significant difference between the groups, 1 = significant difference between the groups.

(MBT-total) and the reactor landfill (rLF). The enthalpy E1 (DM) of the old landfill (oLF-E1) differs significantly from other groups, whereas oLF-E2 is similar to MBT-total-E1 and rLF-E1. By contrast, the enthalpy E2 (ODM) of the old landfill (oLF-E2) differs from all groups, whereas oLF-E1 is similar to MBT-total-E2 and rLF-E2. The development of a stability index based on enthalpy or enthalpy ratios is a future research topic.

3.2. Principal component analysis of DSC-profiles

The efficiency of the biological treatment is reflected by the PCA based on the heat flow profiles (30–950 °C) of MBT-samples (MBT-on and MBT-lf) and materials from a recent reactor landfill (rLF) and an old landfill (oLF) where untreated resMSW and MSW respectively, were deposited. Progressing degradation is visualized along the 1st principal component from the right to the left. Stabilized MBT-materials (MBT-lf) are located in the scores plot next to old landfill samples. The latter are also found among MBT-materials in process, if landfill conditions (e.g., lack of water) have prevented degradation over decades. Samples from the recent reactor landfill are distributed in the group of MBT-materials in process. The position in the scores plot reveals the effect of biological treatment as it shortens the phase of relevant reactivity considerably (Fig. 3).

3.3. Discriminant analysis (PLS-DA)

The divergent composition of MBT-M (30 samples of MSW containing sewage sludge and the biogenic fraction) was confirmed by PLS-DA that was calculated with DSC-profiles (Fig. 4). MBT-M was compared to typical MBT-materials (81 samples) that originated from well-running processes (MBT-C, MBT-D, MBT-J, MBT-O). Well-running processes are characterized by optimum process conditions in terms of air and water supply to guarantee continuous degradation up to the required stability. The deviation

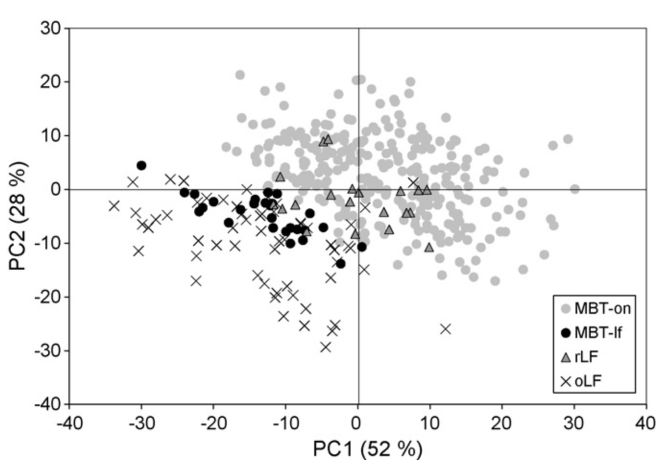

Fig. 3. Scores plot of a PCA based on DSC-profiles of 330 MBT-waste samples (301 MBT-on, 29 MBT-lf), old landfills (oLF, 58 samples) and a reactor landfill (rLF, 20 samples).

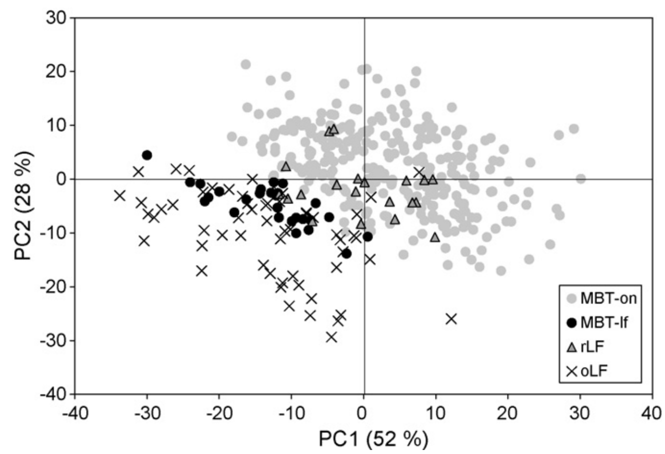

Fig. 4. Differentiation of MBT-materials using DSC-profiles and PLS-DA (MBT-M vs. MBT-C, MBT-D, MBT-J, and MBT-O).

from the typical composition of MBT-waste can reveal insufficient separation of biogenic waste or co-processing of other materials.

3.4. Parameter prediction

Due to the fact that parameters are reflected by the thermal behavior of the material, prediction models were developed, based on the DSC-profiles and a partial least squares regression (PLS-R). Fig. 5 illustrates the prediction models for the calorific value and the TOC. Good correlations (R^2 = 0.94) between thermal data and reference analyses (calorific value and TOC) are obtained. The bias indicates the systematic difference between predicted and measured values and reflects the accuracy of the prediction models. The model parameters (R^2, RMSECV, Bias and RPD) are summarized in Table 5.

Microbial activity in waste materials is strongly related to the stage of decomposition, i.e., to the chemical composition. A prediction model for respiration activity in compost was developed by Meissl et al. [39] using spectral data. A PLS-R based on mass spectra and respiration activities and a PLS-R based on DSC-profiles and respiration activities were calculated. Samples of plant MBT-R where MSW is treated in a different way, rather focusing on stabilization by drying than by biological degradation, and additionally several

Table 5
Model parameters of prediction models for the calorific value, the TOC and RA_4.

	Calorific value	TOC	RA_4 – MS	RA_4 – DSC
Number of samples	147	330	229	229
Thermal data	DSC	DSC	MS	DSC
R^2	0.94	0.94	0.87	0.82
RMSECV	413	1.5	5.4	6.1
Bias	5.2	0.007	−0.003	−0.029
RPD	4.0	4.2	2.7	2.5

R^2 = correlation coefficient, RMSECV = root mean square error of crossvalidation, RPD = ratio of standard deviation to standard error of performance.

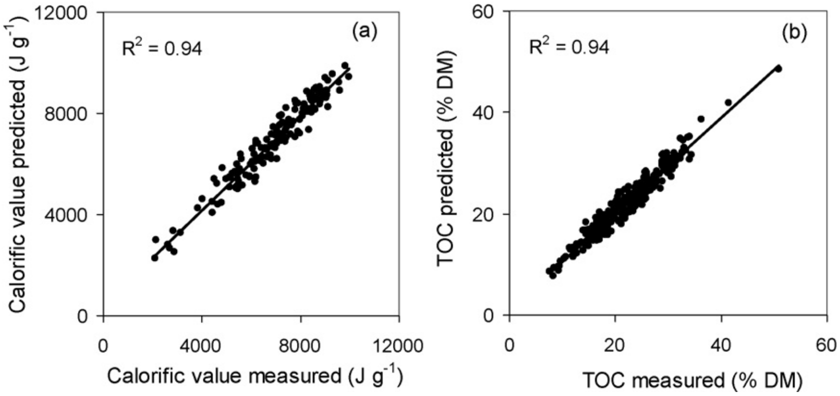

Fig. 5. Prediction of (a) the calorific value and (b) the TOC based on the DSC-profiles and PLS-R.

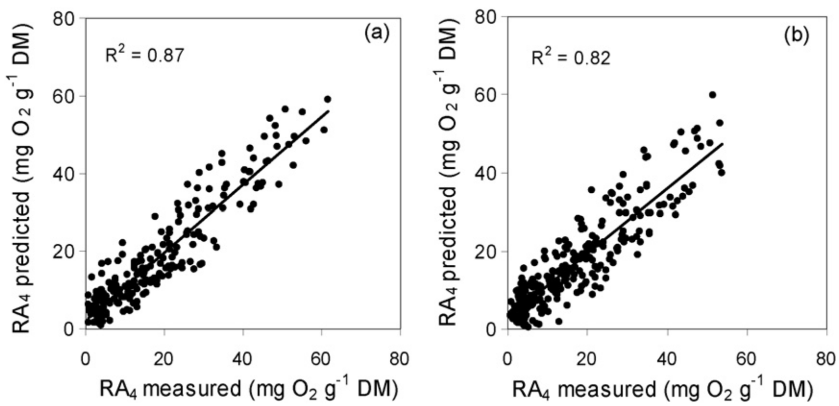

Fig. 6. Correlation between RA_4 and (a) mass spectra of gaseous combustion products and (b) DSC-profiles based on PLS-R.

input materials from other plants were excluded from calculation ($RA_4 > 60\,mg\,O_2\,g^{-1}$ DM). Very reactive samples are not adequately represented by the combustion products.

Fig. 6(a) and (b) displays the correlation between RA_4 and mass spectra and RA_4 and DSC-profiles respectively. Although the correlation between thermal data and RA_4 is weaker ($R^2 = 0.87$ and 0.82 respectively) than the correlation between the calorific value or the TOC and thermal data, the parameter is well reflected by the combustion products and by the DSC-profile. Model parameters are indicated in Table 5. Biological tests and thermal analyses are performed using different sample pools (fresh or dried sample). Moreover, biological tests are more affected by external conditions and therefore error-prone. This might be a reason for the weaker correlation.

The RPD provides information on the accuracy of analyses for a specific purpose. According to Williams and Norris [45] and the AACC Method 39-00 [46] the RPD should be in the following range: ≥2.5 screening in breeding programs; ≥5 acceptable for quality control; ≥8 good for process control, development, and applied research. It should be emphasized that the RPD was developed for prediction of chemical compounds (e.g., proteins, carbohydrates) in cereals by using NIR spectroscopy. Considering the complex composition of MBT-waste and the precision of the reference methods the results obtained are acceptable.

4. Conclusions

Thermal analysis has proven to be a useful method to characterize MBT-waste materials. Biological degradation of municipal solid waste leads to stabilization that has to be verified prior to landfilling. Progressing degradation of municipal solid waste is paralleled by decreasing enthalpies. Further research will focus on the development of a stability parameter based on enthalpy. Evaluation of the substantial data sets recorded by thermal analyses was supported by multivariate statistics. Differentiation of biologically pretreated and untreated municipal solid waste by means of the DSC-profile and a PCA revealed the efficiency of the pretreatment in terms of stabilization time. Residual municipal solid waste that contained a high amount of sewage sludge and biogenic waste could be distinguished from the typical mixture of residual municipal solid waste by discriminant analysis. Prediction of the calorific value and the TOC was based on DSC-profiles and PLS-R. The high coefficient of determination ($R^2 = 0.94$) indicates that these parameters are well reflected by the DSC-profile. A correlation was found between RA_4 and DSC-profiles ($R^2 = 0.82$) and RA_4 and mass spectra ($R^2 = 0.87$). Parameter prediction is useful to replace time-consuming analyses and provides the advantage of simultaneous determination of different parameters. Moreover, additional information regarding material characteristics can be extracted from only one thermo analytical analysis if adequate evaluation tools as presented in the paper are available. The relevant questions in waste management to be answered by thermal analysis focus on material characterization, differentiation of specific input materials, assignment to defined categories (e.g., process operation), process control and parameter prediction. The development of adequate evaluation tools is a prerequisite for the application in waste management practice.

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References

[1] BGBl. Nr. II 39/2008, Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über Deponien (Deponieverordnung 2008), 2008.
[2] M. van Praagh, J. Heerenklage, E. Smidt, H. Modin, R. Stegmann, K.M. Persson, Waste Manage. 29 (2009) 859.
[3] T. Müller, H. Höper, Soil Biol. Biochem. 36 (2004) 877.
[4] P. Rovira, V.R. Vallejo, Soil Biol. Biochem. 35 (2003) 245.
[5] DIN 51900-1, Bestimmung des Brennwertes mit dem Bomben-Kalorimeter und Berechnung des Heizwertes – Teil 1: Allgemeine Angaben, Grundgeräte, Grundverfahren, 2000.
[6] E. Binner, A. Zach, M. Widerin, P. Lechner, Auswahl und Anwendbarkeit von Parametern zur Charakterisierung des Endproduktes aus mechanisch-biologischen Restmüllbehandlungsverfahren, Schriftenreihe des Bundesministeriums für Umwelt, Jugend und Familie, Wien, 1998, p. 147.
[7] M.L. Cayuela, C. Mondini, M.A. Sánchez-Monedero, A. Roig, Bioresour. Technol. 99 (2008) 4255.
[8] F. Bastida, J.L. Moreno, T. Hernández, C. García, Appl. Soil Ecol. 37 (2007) 53.
[9] Y. Chen, Comp. Sci. Util. 11 (2003) 152.
[10] M. Tesar, R. Prantl, P. Lechner, J. Environ. Monit. 9 (2007) 110.
[11] E. Smidt, K. Meissl, J. Tintner, J. Environ. Monit. 9 (2007) 1387.
[12] R. Bäumler, I. Kögel-Knabner, J. Environ. Qual. 37 (2008) 146.
[13] M. Pichler, I. Kögel-Knabner, J. Environ. Qual. 29 (2000) 1337.
[14] D. Said-Pullicino, K. Kaiser, G. Guggenberger, G. Gigliotti, Chemosphere 66 (2007) 2166.
[15] M. Franke, G. Jandl, P. Leinweber, J. Anal. Appl. Pyrol. 79 (2007) 16.
[16] M.F. Dignac, S. Houot, C. Francou, S. Derenne, Org. Geochem. 36 (2005) 1054.
[17] F.J. González-Vila, J.A. Gonzáez-Pérez, K. Akdi, M.D. Gómis, F. Pérez-Barrera, T. Verdejo, Bioresour. Technol. 100 (2009) 1304.
[18] E. Smidt, K.U. Eckhardt, P. Lechner, H.R. Schulten, P. Leinweber, Biodegradation 16 (2005) 67.
[19] M.T. Dell'Abate, A. Benedetti, P. Sequi, J. Therm. Anal. Calorim. 61 (2000) 389.
[20] M.R. Provenzano, N. Senesi, G. Piccone, Comp. Sci. Util. 6 (1998) 67.
[21] M.R. Provenzano, A. Ouatmane, M. Hafidi, N. Senesi, J. Therm. Anal. Calorim. 61 (2000) 607.
[22] P. Melis, P. Castaldi, Thermochim. Acta 413 (2004) 209.
[23] M. Otero, L.F. Calvo, B. Estrada, A.I. Garcia, A. Moran, Thermochim. Acta 389 (2002) 121.
[24] R.G. Brereton, Chemometrics:, Data Analysis for the Laboratory and Chemical Plant, John Wiley & Sons Ltd., Chichester, England, 2002, p. 489.
[25] K. Esbensen, Alborg University, Esbjerg, 2002.
[26] M. Statheropoulos, K. Mikedi, N. Tzamtzis, A. Pappa, Anal. Chim. Acta 461 (2002) 215.
[27] S. Klammer, B. Knapp, H. Insam, M.T. Dell'Abate, M. Ros, Waste Manage. Res. 26 (2008) 173.
[28] R. Zbytniewski, B. Buszewski, Bioresour. Technol. 96 (2005) 479.
[29] M.V. Gil, L.F. Calvo, D. Blanco, M.E. Sánchez, Bioresour. Technol. 99 (2008) 5763.
[30] H. Ecke, Waste Manage. 23 (2003) 631.
[31] B. Scaglia, F. Adani, Sci. Tot. Environ. 394 (2008) 183.
[32] E.V. Mikhailov, O.V. Tupicina, D.E. Bykov, K.L. Chertes, O.Y. Rodionova, A.L. Pomerantsev, Chemom. Intell. Lab. Syst. 87 (2007) 147.
[33] D.F. Malley, C. McClure, P.D. Martin, K. Buckley, W.P. McCaughey, Commun. Soil Sci. Plant Anal. 36 (2005) 455.
[34] M. Hansson, A. Nordberg, B. Mathisen, Water Sci. Technol. 48 (2003) 9.
[35] R. Albrecht, R. Joffre, R. Gros, J. Le Petit, G. Terrom, C. Périssol, Bioresour. Technol. 99 (2008) 448.
[36] H.J. Ko, H.L. Choi, H.S. Park, H.W. Lee, Asian-Aust. J. Anim. Sci. 17 (2004) 1736.
[37] K. Michel, C. Bruns, T. Terhoeven-Urselmans, B. Kleikamp, B. Ludwig, J. Near Infrared Spectrosc. 14 (2006) 251.
[38] P. Capriel, T. Ebertseder, L. Popp, R. Gutser, J. Plant Nutr. Soil Sci., 162, 1999, p. 149.
[39] K. Meissl, E. Smidt, M. Schwanninger, Talanta 72 (2007) 791.
[40] E. Smidt, K. Meissl, M. Schwanninger, P. Lechner, Waste Manage. 28 (2008) 1699.
[41] OENORM S 2123-1, Sampling plans for waste – Part 1: Sampling of heaps, 2003.
[42] E. Smidt, K. Meissl, J. Tintner, Thermochim. Acta 468 (2008) 55.
[43] OENORM S 2027-1, Stability parameters describing the biological reactivity of mechanically biologically pretreated residual wastes – Part 1: Respiration activity (RA_4), 2004.
[44] C.W. Dunnett, J. Am. Stat. Assoc. 75 (1980) 789.
[45] P. Williams, K. Norris, Near-Infrared Technology in the Agricultural and Food Industries, 2nd ed., American Association of Cereal Chemists Inc., St. Paul, 2004, p. 296.
[46] AACC, in Approved Methods of the American Association of Cereal Chemists, Vol. AACC Method 39-00, Ed by American Association of Cereal Chemists (AACC), http://www.aaccnet.org/ApprovedMethods/summaries/39-00-01.aspx, 1999, p. 15.
[47] E. Smidt, J. Tintner, K. Meissl, E. Binner, in: M. Kühle-Weidemeier (Ed.), Proceedings Waste-to-Resources 2009, 3rd International Conference on MBT and Sorting Systems, vol. 64, Hannover, May 12–15, 2009.
[48] L. Sachs, J. Hedderich, Angewandte Statistik – Methodensammlung mit R, Springer-Verlag, Berlin, Heidelberg, 2009, p. 813.