

WASTE MIXTURE COMPOSITION BY THERMOGRAVIMETRIC ANALYSIS

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Abstract

In this work thermogravimetric analysis is applied to examine pyrolysis of single waste components and their blends in order to determine the composition of an unknown waste mixture. The superposition property is assumed, i.e. the mixture thermal degradation curve is obtained as the sum of the curves corresponding to its constituents. The results show that if blended, the individual components are more clearly recognised from the differential mass loss curves. This allows a better identification of the composition. Inaccuracy in determining the composition increases if interactions occur between components, which is the case for PVC–newspaper blend.

Keywords: characterisation, composition, DTG/TG, waste

Introduction

The utilisation of biomass and waste fuels for power production is strongly promoted in the Netherlands. An ambitious goal has been set to increase the share of renewable energy from 1.1% in 1999 to 10% by the year 2020 [1]. Co-combustion in pulverised coal fired plants offers an attractive option because waste and biomass fuels can be efficiently converted to energy. However, the combustion characteristics of secondary fuels are different from that of coal. This can cause operational problems e.g. slagging, fouling, and high temperature corrosion inside the boiler, increased emissions and difficulties in the utilisation of by-products. If the composition of a waste mixture and the effect of a single component were known, it would be possible to predict the combustion behaviour and some of the operational problems might be prevented. A method to determine the composition of a waste mixture is presented hereby.

The pyrolysis and combustion of fossil fuels and biomass is commonly studied using thermal analysis [2, 3]. Thermal analysis as a method to determine mixtures' composition is detailed in literature. In several studies, biomass pyrolysis is expressed as a weighed sum of its macro components, i.e. cellulose, hemicellulose and lignin [4–9]. In other studies, the superposition principle is applied to characterise waste materials; some examples are summarised below.

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Sørum *et al.* [10] investigated several paper and plastic materials by thermogravimetry in order to examine the interaction between different components and detected significant interaction only for the mixture of a cellulosic component and PVC. Fritsky *et al.* [11] developed a methodology to model the devolatilisation of RDF (refuse derived fuel). In their study, kinetic parameters of selected waste components were calculated using the Coats–Redfern method [12] and employed to predict the devolatilisation of a surrogate mixture. The calculated and the experimental mixture mass loss curve were in agreement. The pyrolysis kinetics of paper mixtures was studied by Wu *et al.* [13]. Paper blends were prepared according to their proportional quantities within the domestic waste in Taiwan and the pyrolysis rate of the mixture was satisfactorily expressed as the weighed sum of its individual components. Cozzani *et al.* [14] studied the pyrolysis of RDF and expressed its thermal degradation as a sum of the rates of the main RDF components (paper, polyethylene, and wood). They presented a simple mathematical approach, which determines the fractions of the main RDF components. This approach, the weighed sum method, is also applied in the work presented hereby.

The goal of this paper is to examine waste blends with regard to their composition by thermal analysis. The experimental results described in the following concern mixtures whose major constituents are papers, plastics and wet organic wastes. The pyrolysis behaviour of single waste constituents is measured by a thermogravimetric analyser (TG) and the obtained mass loss curve (TG) or its derivative (DTG) is used as a fingerprint of each component. Synthetic mixtures of individual waste components with a known composition are then prepared. The fingerprints of single components are correlated with that of the mixture using the method presented by Cozzani *et al.* [14] in order to calculate the mixture composition. The weighed sum method is in this work applied to artificial waste mixtures in order to compare the measured and calculated mixture composition.

Experimental

Samples

Single waste components separated from the every-day waste streams in Delft and samples obtained from the Institute of Process Engineering and Power Plant Technology, University of Stuttgart (Germany) were analysed. It should be noted that the components were randomly chosen. Therefore, samples originating from different sources can have somewhat different pyrolysis characteristics. For example, the thermal degradation of various papers depends on the wood types that were used in the paper making process, the use of additives, coatings, bleachers, etc.

Apparatus and measurement procedure

A thermobalance SDT 2960 manufactured by TA Instruments operating at simultaneous DTA-TG mode was used. The equipment has a horizontal dual-beam design

and is therefore capable of simultaneous measurements; only TG data are reported here. Samples from Delft waste stream were cut into pieces of 1–2 mm and those obtained from Stuttgart were received already ground to a sample size of 1.5 mm. A quantity of 10 ± 0.5 mg sample material was evenly distributed on an open alumina sample pan and heated at a constant rate of 20 K min^{-1} up to 900°C while the thermobalance was continuously purged with nitrogen (100 mL min^{-1} , STP). The TG-results reported here are normalised with the mass of the sample at 150°C to eliminate the effect of moisture. The mixtures were prepared by placing the least thermally stable component on the bottom of the sample cup and adding the other components in the order of increasing thermal stability. The mixing between compounds was therefore maximised [10]. The measurements of single components and mixtures were repeated twice; it was nevertheless not possible to prepare mixture replicates with exactly the same composition.

Results and discussion

Single components

Single waste components characterised by the TG include newspaper, banana peel, wood (pine), PVC (polyvinyl chloride), PET (polyethylene terephthalate), and HDPE (high-density polyethylene). All components are commonly present in RDF and municipal solid waste. Table 1 shows the proximate analysis of these samples and Fig. 1 depicts their TG- and DTG-graphs.

Table 1 Proximate analysis of pure components in mass% (as received)

Sample	Moisture	Volatile matter	Fixed carbon	Ash (ashed at 550°C)
Banana peel	7.4	57.6	18.9	16.1
HDPE	0.3	99.3	0.2	0.2
Newspaper	5.4	79.4	14.1	1.1
PET	0.4	85.4	14.2	0.0
PVC	0.2	91.2	8.6	0.0
Wood	5.5	78.0	16.3	0.2

Paper and wood are major constituents of municipal solid waste in most countries [15]. Wood mainly composes of cellulose, hemicellulose and lignin, which, in different fractions, are also the major compounds of papers. Newspaper is manufactured by mechanical pulping, i.e. by grinding it without addition of chemicals, from bark stripped wood. The TG-curves of newspaper and wood (Fig. 1a) are almost overlapping because newspaper, due to mechanical pulping, includes all the major wood components. The main DTG-peak of wood and newspaper takes place around $370\text{--}380^\circ\text{C}$ and corresponds to the decomposition of cellulose. The shoulder on the left side of the main DTG-peak is more clearly observed for wood and is caused by

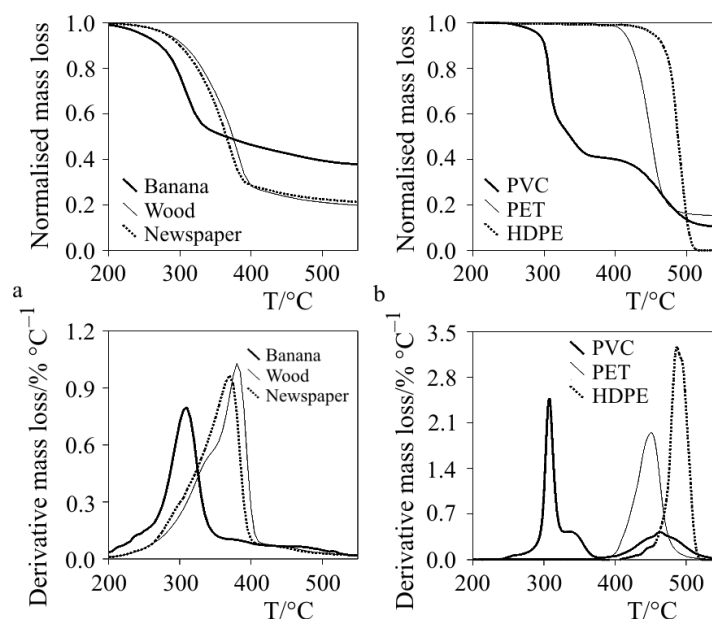


Fig. 1 TG- and DTG-curves of pure components, a – organic/cellulosic compound; b – plastics

the degradation of hemicellulose [4, 10]. The long tailing section on the right of the main peak of both newspaper and wood corresponds to the decomposition of lignin.

The banana peel sample was pre-dried before the TG experiment in order to remove most of its moisture. As Fig. 1a depicts, banana starts decomposing earlier than the cellulosic compounds reaching its maximum rate of mass change already at 310°C. The main compound of banana is starch [16] and therefore the cellulose degradation is observed as a hardly recognisable peak around 370°C. In another study, starch was devolatilised at the same heating rate as in this work and the maximum pyrolysis rate was indeed measured at about 300°C [17].

Plastics are polymers consisting of long molecule chains, which in most western-world countries have a large share in municipal solid waste. They have a high heating value and therefore greatly contribute to the amount of energy released during waste combustion. As observed in Fig. 1b, HDPE reaches the maximum rate of mass loss at 490°C and devolatilises almost completely in one step; the small char yield is presumably caused by colours and additives. The pyrolysis of PET and PVC left notable amounts of char in the sample cup. PET degrades in one step with the maximum rate at 450°C, while PVC decomposes in two steps. At about 310°C PVC loses its chlorine forming HCl [18] and the second step between 400 and 500°C corresponds to the degradation of the remaining hydrocarbon residue [10].

Artificial waste mixtures

The simplest approach to correlate the thermal decomposition curve of a mixture to those of its single components is the Weighed Sum Method (WSM). It assumes a linear behaviour of the mixture with respect to the mass fractions of its constituents, which is mathematically formulated as [14]

$$Y_{\text{mix}} = x_1 y_1 + \dots + x_n y_n = \sum_{i=1}^n x_i y_i \quad (1)$$

where Y_{mix} is the calculated value at the TG- or DTG-mixture curve and y_i the measured value at a TG- or DTG-curve of constituent i . The coefficients x_i are unknown i.e. the mass fractions of each component i in the mixture. n is the number of compounds taken into account. For the x_i in Eq. (1), the least squares method is used to minimise the difference between the measured and the calculated values. The objection function is S_R , defined as:

$$S_R = \sum_{N_{\text{data}}} [y_{\text{mix}} - y_{\text{mix}}]^2 = \sum_{N_{\text{data}}} \left[y_{\text{mix}} - \sum_{i=1}^n x_i y_i \right]^2 \quad (2)$$

where y_{mix} is the measured value at a TG- or DTG-mixture curve and N_{data} the amount of data points taken into account. The WSM is applied separately to the TG- and the DTG-curves. The Excel add-in Solver is used for the multivariable constrained minimisation.

To test the WSM, synthetic mixtures containing four waste compounds were prepared. Several synthetic mixtures were analysed but only two of them are discussed here due to the limited space. The first mixture consists of newspaper, banana peel, PET, and HDPE; Fig. 2 shows two replicate measurements of this mixture. The uppermost bar in each graph shows the measured mixture composition. In Fig. 2a, approximately 25% of each component is mixed, whereas in Fig. 2b almost 50% of the mixture is banana. Besides the measured composition, the calculated compositions based on TG- and DTG-curves are shown. As it is displayed in Fig. 2a, both TG- and DTG-curves allow for an accurate estimation of single component shares. On the contrary in Fig. 2b, it can be noted that composition analysis based on TG-curves results in an increased contribution of banana while the calculated share of newspaper is 0%. The TG-curves of banana and newspaper have a similar shape and slope but banana starts decomposing at a temperature that is about 30°C lower than newspaper; therefore the WSM applied on TG-data cannot distinguish between the components. The DTG-curves, however, predict the mass

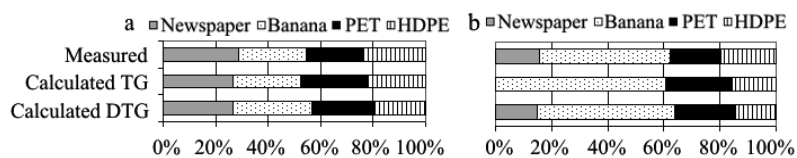


Fig. 2 Measured and calculated mass fractions of single components in newspaper-banana-PET-HDPE mixture

fractions properly also for case in Fig. 2b. This can be explained by the DTG-peak temperatures, which are 310 and 375°C for banana and newspaper, respectively. Such a difference is more recognisable when applying the weighed sum method. This suggests that DTG-curves are more suitable for the composition determination. In both cases, the fractions of PET and HDPE are acceptably calculated.

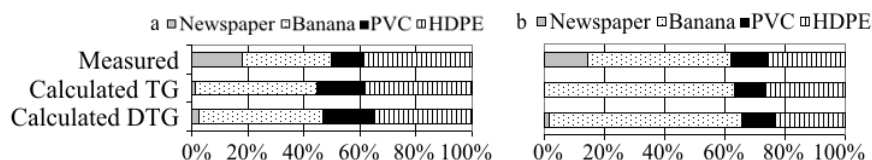


Fig. 3 Measured and calculated mass fractions of single components in newspaper–banana–PVC–HDPE mixture

PET in the four-component mixture was replaced by PVC and the measurements were repeated. In both cases shown in Fig. 3, the WSM applied on the TG- and DTG-curves underestimates the share of newspaper and overestimates that of banana. The fraction of PVC is exaggerated for case in Fig. 3a, while it is reasonably estimated for case in Fig. 3b. The WSM manages to provide a good indication of the HDPE content of the blend. Explanation for the errors in the calculated single component fractions is in the following examined by comparing the measured, calculated and theoretical mass loss curve of the mixture of case in Fig. 3b.

Figure 4 displays three different DTG-curves of newspaper–banana–PVC–HDPE mixture (Fig. 3b): measured, theoretical and calculated. The theoretical mixture curve is defined as the ideal mixture DTG-curve if there were no interactions between components and it is obtained from the measured single component fractions and measured single component DTG-curves. The calculated curve is obtained based on the calculated single component fractions and measured single component DTG-curves. In Fig. 4, the theoretical DTG-curve shows a clear shoulder on the right side of the first degradation peak, between 340–390°C. In the measured curve, this shoulder is disappeared and the first decomposition peak is higher. Comparing the curves in Fig. 4 with the single com-

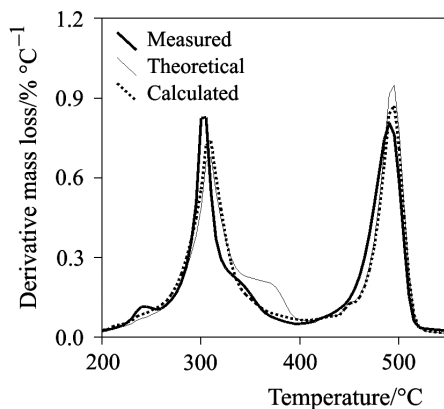


Fig. 4 DTG-curves of banana–newspaper–PVC–HDPE mixture, case in Fig. 3b

ponent curves in Fig. 1 shows that the shoulder in the calculated curve around 370°C is the fingerprint of newspaper. In addition, PVC has a smaller peak attached to the right of its first decomposition peak, which also cannot be observed in the measured mixture DTG-curve. This implies that newspaper and PVC react with each other when mixed. The mixture therefore decomposes at a lower temperature than its components alone i.e. the mixture decomposition rate is accelerated. As a consequence, the WSM, assuming linear behaviour of a blend with respect to the contributions of its individual compounds, is not valid. Also other authors [10, 19, 20] have observed interaction between PVC and cellulose, which is the major constituent of newspaper. It is suggested that these interactions are enhanced in a thermogravimetric analyser because PVC and newspaper start decomposing at similar temperatures and therefore not only H and Cl radicals released from PVC but also devolatilisation products from newspaper are present during pyrolysis.

The change in the reactivity of a PVC/newspaper mixture was further investigated because the PVC contents of real waste mixtures are considerably lower than in the artificial mixture described in this work, usually in the range of a few percent. A series of measurements with a decreasing PVC-content was carried out: 25.7, 12.9, 6.7 and 2.6% of PVC, the rest being newspaper. The WSM was applied first to TG-curves and then to DTG-curves. As Fig. 5 shows, the measured and calculated TG-curve come closer to each other with decreasing PVC content. However, by examining the measured and modelled mass fractions it can be noted that the calculated PVC content is in all cases overestimated. In the first case (Fig. 5a), the measured PVC content is 25.7 but 57.1% of PVC is calculated instead. In the case with the lowest measured PVC content of 2.6% (Fig. 5d), the WSM method determines 8.4% of PVC. Observing only the graphs in Fig. 5a–d, a conclusion could be drawn that the

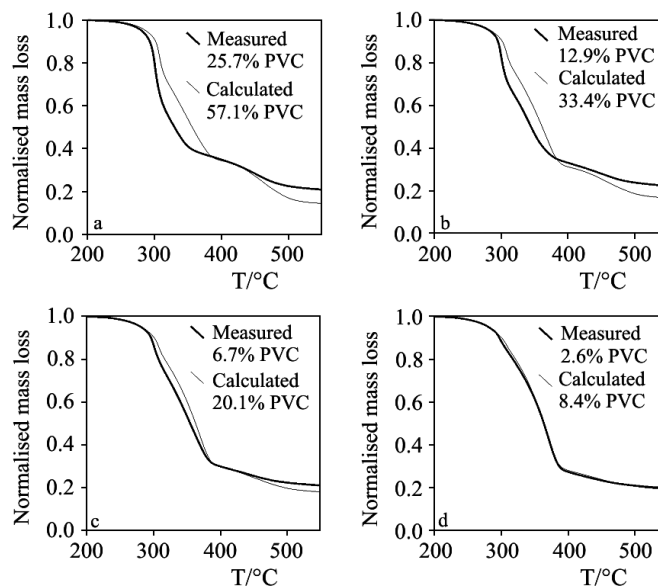


Fig. 5 TG-curves of PVC/newspaper mixture with decreasing PVC content. a – 25.7% PVC (the rest newspaper); b – 12.9% PVC; c – 6.7% PVC and d – 2.6% PVC

lower the PVC fraction in newspaper/PVC blend, the better the fit between the measured and the modelled TG-curve. This is, however, misleading because the relative error between the measured and calculated PVC share actually increases when the fraction of PVC decreases.

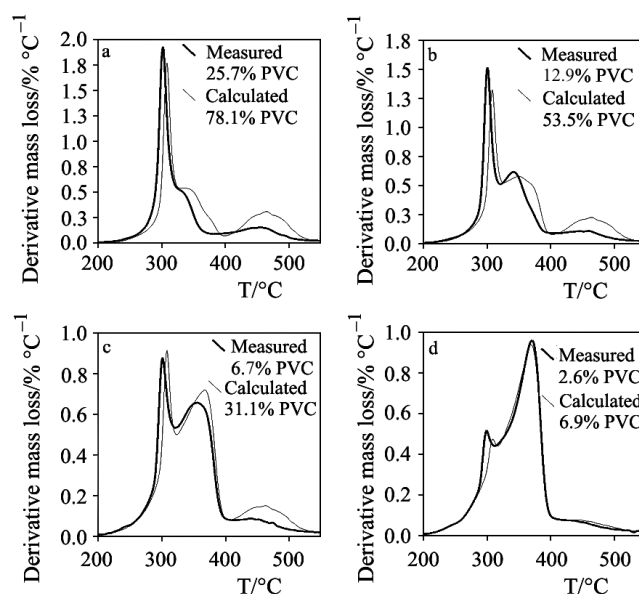


Fig. 6 DTG-curves of PVC/newspaper mixture with decreasing PVC content. a – 25.7% PVC (the rest newspaper); b – 12.9% PVC; c – 6.7% PVC and d – 2.6% PVC

The DTG-curves of the PVC–newspaper mixtures discussed above are shown in Fig. 6. The share of PVC is even less accurately determined based on DTG-curves, the only exception is the case of 2.6% PVC (Fig. 6d). At low PVC concentrations (2.6 and 6.7%), both peaks of newspaper and PVC are still observed in the blend DTG-curve. However, already for the mixture of 12.9% of PVC, the peak of newspaper at 370°C is hardly visible and for the blend of 25.7% of PVC it is vanished. The comparison of the measured and calculated PVC fractions for case in Fig. 6c shows that the WSM predicts more than four times the measured PVC content. However, if only observing the fit of the measured and modelled DTG-curves, the correlation of the curves seems acceptable. Like noted in the previous paragraph, based on the rather good fitting of the curves, it is not obvious that the error in the calculated PVC fraction is rather high. These examples demonstrate that even small fractions of PVC mixed with a cellulosic compound can lead to large errors in the calculated mixture composition.

Conclusions

The pyrolysis behaviour of single waste components and their blends is characterised with a thermogravimetric analyser and the obtained TG- or DTG-curves are used as

fingerprints of each material. The thermal degradation behaviour of artificial waste mixtures is correlated with that of the single constituents using a superposition principle. It is shown in this paper that the weighed-sum method is appropriate for materials, whose TG- or DTG-curves significantly differ from each other. However, if the degradation graphs of two materials have a similar shape and slope, it is difficult to distinguish between them. In general, modelling with DTG-curves gives better results than modelling with TG-curves. In presence of PVC and a cellulosic compound, the WSM gives larger errors because the mixture reacts at lower temperatures than either of its components alone. Consequently, the fractions of single components are not correctly predicted even for low PVC contents. In the future, the waste characterisation work will be continued by including more waste compounds in the study.

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