



# Pyrolysis characteristics of excavated waste material processed into refuse derived fuel



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## HIGHLIGHTS

- We study the thermal degradation behavior of excavated (i.e. aged) waste material.
- Refuse derived fuel (RDF) is subject to thermogravimetric analysis.
- Experiments are combined with Matlab optimization study to determine kinetic parameters.
- The thermal degradation behavior of the RDF was modeled assuming four parallel reactions.
- A comparison is made with fresh waste material and other biomass sources, the agreement is good.

## ARTICLE INFO

### Article history:

Received 14 October 2013

Received in revised form 12 November 2013

Accepted 7 January 2014

Available online 22 January 2014

### Keywords:

Refuse derived fuel  
Enhanced landfill mining  
Pyrolysis  
TGA  
Kinetics

## ABSTRACT

The pyrolysis characteristics of refuse derived fuel (RDF) processed from excavated landfill waste are investigated by thermogravimetric analysis combined with a MATLAB<sup>®</sup> optimization study to determine chemical kinetic parameters. Waste samples – a mix of municipal and industrial waste – with particle sizes between 150 and 250  $\mu\text{m}$  are heated to 800 °C at a heating rate of 10 °C  $\text{min}^{-1}$ . The independent parallel first-order reactions model is used for the kinetic analysis. Four parallel reactions describe the thermal degradation behavior of the waste material. The calculated kinetic parameters (activation energy  $E = 100, 149, 99, 353 \text{ kJ mol}^{-1}$ , resp.) for the four identified fractions (hemicellulose, cellulose, and two types of plastic) did not fully agree with experimental studies available in the literature for fresh waste materials. The first fraction closely resembles hemicellulose. The second fraction is similar to cellulose, but the broad peak could indicate that lignin degradation is also covered. The behavior of the third fraction (i.e. the least stable plastics) deviates from literature data. This is explained by the partial overlap between the decomposition range of the second and third fraction. The fourth fraction decomposes in the same way as the stable plastics. The characteristics of the excavated waste (composition, age, possible catalytic effect of mineral matter and metals, etc.) could provide an explanation for the differences observed when comparing with fresh waste.

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## 1. Introduction

There is an ever increasing concern for our ecosystem. This environmental awareness grows as more and more attention is paid to threats posed by greenhouse gas emissions and their presumed contribution to climate change. Developing countries are joining the race for economic development, leading to more industrialization which in turn increases emissions of greenhouse gases and other pollutants. The widespread availability of biomass and

waste – renewable fuels and potentially neutral in relation to global warming [1] – motivates the extensive research carried out in the past decades for the development of advanced thermochemical conversion technologies [2,3]. Mathematical modeling is a useful tool for process design and optimization, but the reliability of the results is highly dependent on an adequate description of chemical and physical processes, and the correctness of input data. In this context, the solid fuel devolatilization kinetics play an important role. This is explained by the fact that pyrolysis is not only an independent conversion technology, but also comprises a key step in gasification and combustion processes [4].

In the present work thermogravimetric analysis is employed for a systematic investigation of the pyrolysis characteristics of excavated waste, i.e. waste materials which have previously been

Abbreviations: ELFM, Enhanced Landfill Mining; RDF, refuse derived fuel; MSW, municipal solid waste; IW, industrial waste.

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### Nomenclature

$A$	preexponential factor ( $\text{min}^{-1}$ )	$N$	number of independent reactions
$c_i$	fraction of volatiles produced by the $i$ th component	$R$	universal gas constant ( $8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$ )
$E$	activation energy ( $\text{kJ mol}^{-1}$ )	$S_{DTC}$	objective function
$m_0$	initial dry sample mass (mg)	$T$	temperature ( $^{\circ}\text{C}$ or $\text{K}$ )
$m_{char}$	final char yield (mg)	$\alpha$	conversion (reacted fraction)
$m_i$	actual sample mass of component $i$ (mg)		

landfilled. The valorization of excavated waste materials (as materials or as energy) is the main objective of Enhanced Landfill Mining (ELFM) [5]. The successful implementation of Waste-to-Energy (WtE) technologies in the concept of ELFM depends on the WtE process efficiencies, which are in turn dependent on the quality of the waste feed. The characteristics of solid waste feedstock are influenced by various factors ranging from storage method (influence on humidity), maturity (large range for excavated landfill waste), sorting policy (differs from country to country) and many more [6]. Previously landfilled materials constitute an important waste stream in the loop-closing concept.

Due to the heterogeneous nature of the waste streams in landfills, specific treatment and separation schemes are required to enable the generation of valuable (recycled) materials. The combustible fraction of waste streams that does not qualify for material recovery or recycling, is processed into refuse derived fuel (RDF) by means of shredding, mesh screening, cyclone separation, magnetic separation, scrubbing, and density separation. The resulting high energy density fuel can serve as an input to WtE plants. In case of ELFM, the separation and treatment processes should go a step further than what is currently accomplished at existing waste treatment plants. The treatment scheme should be able to recycle and recover materials from a mixture of heterogeneous waste streams. The composition of the aged waste, and hence its physical and chemical properties, are influenced by the age of the waste and the degradation of the waste over time. A recent case study [6] has shown that despite these complications, the production of a high quality RDF from excavated waste streams is feasible. The most important observations that were made when comparing fresh and aged municipal solid waste are briefly repeated here. The amount of glass, metal, inert, textiles, paper/cardboard and plastics compares well between the fresh and aged waste. An organic fraction is no longer present in the aged waste samples and has most likely degraded into the fines fraction ('soil type waste') of the aged sample. It might seem surprising that the paper/cardboard fraction has not degraded further over such a long period of time. This is due to the fact that most landfills are fundamentally anaerobic because they are compacted so tightly, and thus do not let much air in [7]. Any biodegradation that does take place, does so very slowly. In another study [8], it is reported that only 5–10% of cellulose is degraded in nature under anaerobic conditions.

The plastics and paper/cardboard fractions in the aged waste display higher ash fractions than their fresh counterparts. The large fraction of fines present in the excavated waste is partially explained by the thermal degradation of the waste over time. These fines also display a high ash content (around 20%). These two factors combined, provide an explanation for the high ash content (approximately 22%) found in the RDF processed from aged waste. According to a European report, the ash content in RDF processed from fresh waste (ranging from municipal waste to demolition waste) varies from 7% to 20% [9]. Pyrolysis studies available in the literature [10,11] have investigated RDF materials with an ash content from 10% up to 15%.

The implementation and commercialization of state-of-the-art WtE technologies using excavated waste as feedstock require input

data related to the physicochemical processes taking place, essential for generating meaningful numerical simulation results. The pyrolysis kinetic parameters of excavated waste materials constitute an essential part of the required input data.

Numerous studies have already investigated the pyrolysis of biomass and lignocellulosic materials [12–14], while others focused on the pyrolysis of 'fresh' waste components [11,15–17]. As Gronli et al. [1] reported, the derived kinetic parameters depend on the specific pyrolysis conditions, i.e. temperature profile, heating rate, pressure, particle size, ambient gas environment, and the presence of ash or mineral matter. Several researchers have extensively studied the catalytic role of the inorganic matter and its effect on the kinetic parameters [13,18–21]. However, to date, very little research has been performed on excavated waste material.

Thermogravimetric analysis (TGA) has proven to be a reliable tool for the systematic investigation of the chemical kinetics of biomass and waste material for low heating rates. The small sample size and strict monitoring of experimental conditions during TGA ensure that transport processes do not hinder the study of the chemical kinetics. The kinetic data obtained under strict kinetic control can be coupled with heat and mass transfer models for the simulation of practical thermochemical conversion systems. Kinetic parameters are usually calculated using a model of independent parallel first-order reactions. The underlying assumption is that the thermal degradation curve of the complex material is the sum of the contributions of the corresponding pseudocomponents, which react through independent parallel reactions. However, other kinetic models (e.g. competitive reactions, successive reactions, etc.) have also been postulated [21].

The main objectives of this work are (a) to determine the pyrolysis kinetic parameters for excavated waste, to the authors' knowledge the first analysis for this type of material, and (b) to compare these results with data found in the literature for 'fresh' waste materials.

## 2. Experimental

### 2.1. Materials

Thermogravimetric analyses were performed on RDF processed from excavated waste which, in this case, is a combination of municipal solid waste (MSW) (59%) and industrial waste (IW) (41%). The proximate and ultimate analyses are summarized in Table 1. The compositional analysis is also shown, it provides a rough estimation of the different material types the waste is composed of. The enhanced landfill mining potential of these waste materials was assessed in a recent case study [6]. Furthermore, the methods followed to excavate and characterize the landfill waste are thoroughly explained. It was found that the storage time of the MSW varied between 14 and 29 years; while for the IW, storage time varied between 14 and 24 years. For more detailed information, the authors refer to the work performed by Quaghebeur et al. [6].

**Table 1**

Proximate, ultimate and compositional analysis of RDF processed from excavated waste (59% municipal waste, 41% industrial waste).

Proximate analysis (wt% dry)		Ultimate analysis (wt% dry)		Compositional analysis (wt%)	
Moisture	4.6	C	46.8	Plastics	47
Fixed carbon	8.6	H	5.7	Wood + paper	24
Volatile matter	69.3	O <sup>a</sup>	22.3	Textiles	10
Ash	22.1	Cl	1.60	Fines	18
		N	1.25		
NCV (MJ/kg <sub>dry</sub> )	22.37	S	0.26		

<sup>a</sup> By difference.

In order to get a better understanding of how the waste composition determines the thermal degradation behavior, the two waste fractions (*i.e.* municipal and industrial waste) have also been analyzed separately. The results are summarized in Table 2. The variations in proximate and ultimate analyses, between these two fractions, are not significant. It is however surprising to see that the values from the proximate and ultimate analyses of the mixed RDF are not in between those of the separate fractions, despite the fact that care was taken to obtain as representative samples as possible. More specifically, large volumes of the separate waste fractions were milled to *mm*-range prior to mixing and sampling. It could be possible that the final sample was still not homogeneous enough due to the highly heterogeneous character inherent to waste material, regardless of the precautions taken.

The compositional analysis of the mixed RDF material indicates a plastics content of 47% (see Table 1), a relatively large fraction when compared to the RDF materials studied by other researchers [16,22] as they report plastic fractions varying from 16% to 26%. However, this is easily explained by the high plastics fraction found in the industrial waste (66%, see Table 2), in addition to the high amount of industrial waste (41%) used to produce the mixed RDF material.

## 2.2. Apparatus and procedure

A stepwise procedure was followed to obtain representative samples for the TGA analyses. In the first step, waste samples were taken from a large batch of RDF material (particle size 1–25 mm) and collected in buckets. This RDF had already gone through a series of sorting/drying/shredding routines, which resulted in a relatively homogeneous batch of material as compared to the waste 'as received' from landfills. In the second step, these samples were oven dried at 60 °C for 24 h. Afterwards, part of the collected material was milled (centrifugal mill) to obtain 1–2 mm particles. In the last step, part of the *mm*-range material is milled further to 150–250 μm particle size, a range suited for TGA analyses. Thermogravimetric experiments were performed on a TA Instruments 951–2000 apparatus (temperature range from 25 to 1150 °C). Small samples (20 mg) were placed in an open quartz sample pan to reduce the effects of possible side reactions and heat and mass transfer limitations. Before the heating program was

initiated, the system was purged for 20 min with high purity helium to ensure an atmosphere free of oxygen. The thermogravimetric experiments started with a drying session: the sample was heated up to 120 °C at a heating rate of 20 °C min<sup>-1</sup> and ended with an isothermal period of 50 min. The subsequent thermal decomposition was carried out at a slow heating rate (10 °C min<sup>-1</sup>, with helium at 100 ml min<sup>-1</sup>) up to the final temperature (800 °C) and an isothermal period of 5 min.

In order to check the repeatability of the experiments, one experiment is repeated three times and the corresponding weight loss and temperature profiles are compared. The repeatability check is performed on 20 mg samples with dry air as purge gas (flow rate of 100 ml min<sup>-1</sup>) at a heating rate of 5 °C min<sup>-1</sup>. The experiments start with a 20 min drying period at 110 °C. Fig. 1 shows the weight loss versus temperature curves for the three experiments. It clearly shows the results agree very well, confirming their repeatability. This also holds for the DTG results, not shown here. It should be noted that most of the experiments were performed at a heating rate of 10 °C min<sup>-1</sup>. However, the experimental repeatability was found to be equally good as for the experiments performed at a lower heating rate. Nevertheless, to ensure that consistent results were obtained, TGA experiments for the

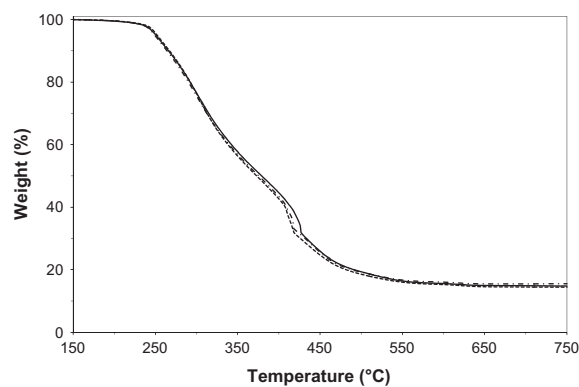


Fig. 1. Weight loss as a function of temperature for RDF in dry air: repeatability check.

**Table 2**

Proximate, ultimate and compositional analysis of separate RDF waste fractions (MSW and IW).

Proximate analysis wt% dry	Ultimate analysis wt% dry		Compositional analysis wt%					
	MSW	IW	MSW	IW	MSW	IW		
Moisture	2.5	7.0	C	51.9	55.2	Plastics	36	66
Fixed carbon	10.8	10.5	H	6.5	6.6	Wood + paper	36	5
Volatile matter	72.2	71.7	O <sup>a</sup>	21.8	16.5	Textiles	15	2
Ash	17.0	17.8	Cl	1.30	2.10	Fines	13	26
			N	1.33	1.43			
NCV (MJ/kg <sub>dry</sub> )	22.80	23.65	S	0.20	0.39			

<sup>a</sup> By difference.

three different types of RDF used (mixed, MSW, IW) were repeated at least three times.

### 2.3. Pyrolysis kinetic model

The pyrolysis of biomass and waste is a complex process with a multitude of parallel and competitive reactions taking place simultaneously. The shoulders and/or double peaks on the DTG curves reveal this complexity. However, DTG profiles obtained from the pyrolysis of waste samples can essentially be described by the relatively simple independent parallel, first-order reaction model. It is assumed that the thermal degradation of the complex material is the sum of the contributions of the corresponding pseudocomponents, which react through independent parallel reactions. Earlier studies have shown this approach is successfully applied for different types of biomass and wastes [12,13,15,21].

The rate of conversion for a single component is described by Eq. (1)

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha) \quad (1)$$

$A$  and  $E$  are the frequency factor and activation energy, respectively.  $\alpha$  is the conversion (reacted fraction) which is expressed by Eq. (2)

$$\alpha = \frac{m_0 - m}{m_0 - m_{char}} \quad (2)$$

$m_0$ ,  $m$  and  $m_{char}$  are the initial sample mass, actual sample mass and char yield (including ash), respectively.

If the material consists of more than one component and one assumes that each component reacts independently from the others, then the overall rate of conversion for  $N$  reactions can be described by Eq. (3)

$$-\frac{dm}{dt} = \sum_i c_i \frac{d\alpha_i}{dt} \quad i = 1, 2, \dots, N \quad (3)$$

The separate conversion  $\alpha_i$  for each component is given by Eq. (4)

$$\alpha_i = \frac{(m_{0,i} - m_i)}{(m_{0,i} - m_{char,i})} \quad (4)$$

The coefficient  $c_i$  expresses the contribution of each partial process to the overall weight loss, in other words it represents the fraction of volatiles produced by the  $i$ th component, given by Eq. (5)

$$c_i = m_{0,i} - m_{char,i} \quad (5)$$

For the kinetic analysis, nonlinear least squares (NLS) algorithms (Levenberg–Marquardt, MATLAB<sup>®</sup>) are used that identify the parameters ( $A_i$ ,  $E_i$ , and  $c_i$ ) that minimize the least squares sum  $S_{DTG}$  presented by Eq. (6)

$$S_{DTG} = \sum_{j=1}^N \left[ \left( \frac{dm}{dt} \right)_j^{\text{exp}} - \left( \frac{dm}{dt} \right)_j^{\text{calc}} \right]^2 \quad (6)$$

To ensure that a physically meaningful result is obtained, the volatiles fractions ( $c_i$ ) should sum up to one. This constraint is taken into account when solving the optimization problem.

## 3. Results and discussion

This section discusses the degradation characteristics of the RDF samples, experimental findings are compared to results found in the literature. Then, the estimated kinetic parameters are presented. These kinetic parameters result from an optimization

routine that compares the measured weight loss curves to the calculated curves composed of a set of parallel first order reactions. Finally, measurements and predictions are compared.

### 3.1. Decomposition characteristics of RDF

Fig. 2 displays the mass fraction  $Y$  ( $m/m_0$ ) and the time derivative of the mass fraction  $-dY/dt$  (indicated as TG and DTG curves, resp.) as a function of temperature, for the three different types of RDF material. The DTG profile for the mixed RDF sample exhibits two small, partly overlapping, peaks located in the temperature region of 250–380 °C, and one large asymmetric peak with a soft shoulder around 450 °C. The low (<400 °C) and high (>400 °C) temperature behaviors are attributed to the devolatilization of the lignocellulosic and the plastics fraction of the waste material, respectively. The temperature intervals of hemicellulose and cellulose decomposition partially overlap, which explains why the hemicellulose decomposition (less stable component) usually appears as a more or less pronounced shoulder instead of a well-defined peak [1]. However, the experimental results for the RDF samples exhibit two separate peaks (at 285 °C and 352 °C, resp.) for these components. Fahmi and his colleagues [23] found similar results in their research on the influence of metals on the pyrolysis characteristics of lignocellulosic feedstock. They noticed a strong catalytic effect of metals (especially alkali metals) on the decomposition behavior of (hemi)cellulose. The metal analysis of the RDF samples studied here indicates that they contain a variety of metals, see Table 3. It would, however, require more data on the metal content of RDF from other sources to verify if there is indeed a catalytic effect of metals (and/or inorganics) on (hemi)cellulose degradation. Due to a lack of literature data, it is not feasible at this moment to confirm or disprove this hypothesis, more extensive research is required.

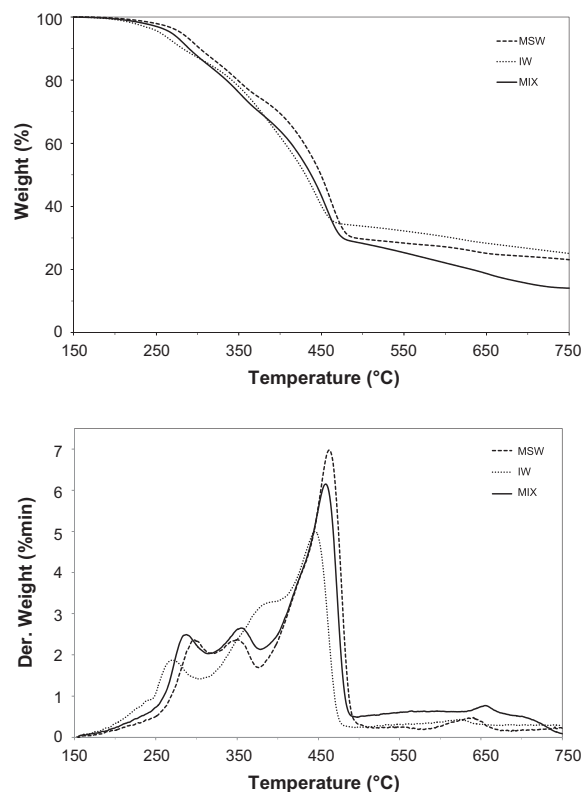


Fig. 2. Weight loss (%), left) and rate of weight loss (%/min, right) as a function of temperature for three different types of RDF in helium (heating rate 10 °C/min).

**Table 3**  
Metal analysis of mixed RDF material.

	mg/kg <sub>dry</sub>
Barium	1600
Lead	1100
Chromium	250
Copper	1400
Manganese	190
Molybdenum	10
Nickel	110
Phosphorus	430
Silicon	30000
Zinc	2900
Aluminum	6100
Calcium	20000
Iron	24000
Sodium	600
Potassium	560
Magnesium	2200

At higher heating rates (20 and 40 °C min<sup>-1</sup>), it is observed that the two peaks merge into a single peak. This can be explained by thermal lag. At higher heating rates, heat transfer resistances can only be eliminated by using very small sample masses (≈1 mg) [13].

Lignin, the third component found in lignocellulosic material, decomposes over the same temperature range as hemicellulose and cellulose. Consequently, lignin does not appear as a separate peak in the DTG curve.

Plastics comprise an important fraction in RDF, setting it apart from the more commonly investigated biomass materials. The plastics present in RDF are mainly polyethylene (PE), polyethylene terephthalate (PET), polyamide (PA), polypropylene (PP), polycarbonate (PC), polystyrene (PS) and polyvinylchloride (PVC). These plastics devolatilize in one step, over the temperature range of 400–550 °C. PVC forms an exception, the multi-stage degradation of PVC can roughly be divided in a first stage dehydrochlorination step (320 °C), forming a thermally stable char which decomposes further in a second step (470 °C) [10]. The high temperature region of the DTG curve shown in Fig. 2 displays a rather broad peak (at 456 °C), indicating there is a wide range of plastics present in the waste material. Of course, this could be expected when combining household waste (packaging material, tetra pack, mainly PE) and industrial waste (construction material, such as PVC piping, polyurethane foam).

As mentioned before, the two waste fractions (MSW and IW) have also been analyzed separately, results are shown in Fig. 2. The DTG profile of the mixed RDF sample is almost identical to the profile found for MSW-RDF. The differences worth mentioning are the shift (mix compared to pure MSW) of the first peak (hemicellulose) to lower temperatures ( $\Delta = 10^\circ$ ), as well as the shift of the plastics peak to lower temperatures ( $\Delta = 5^\circ$ ). The thermal degradation of both fractions in the IW-RDF (*i.e.* lignocellulosic and plastic) starts at lower temperatures compared to MSW-RDF. Therefore, the DTG profile of the mixed RDF lies somewhere in between the DTG profiles of the pure samples. It is clear from Fig. 2 that the IW-RDF behaves differently, there are only two distinct peaks and the second peak has a very broad shoulder on the left side. The first peak occurs at quite low temperatures (268 °C) compared to the temperatures reported in the literature for lignocellulosic degradation [12]. Hemicellulose (the least stable component) usually decomposes around 300 °C. Compared to the relatively sharp plastics peak seen for mixed RDF and MSW-RDF, the peak for IW-RDF is broad and blunt, occurring at lower temperatures (*i.e.* 443 °C compared to 460 °C). The overlap between lignocellulosic and plastics degradation is more pronounced for the IW-RDF than for the MSW-RDF and mixed RDF. Despite the fact that

the proper measures were taken to obtain representative samples, the mixed samples might not contain the anticipated amount of the separate waste fractions. The different behavior observed for municipal and industrial waste can be attributed to the different types of materials found in these waste streams, especially as far as the plastics fraction is concerned.

### 3.2. Kinetic model and parameters

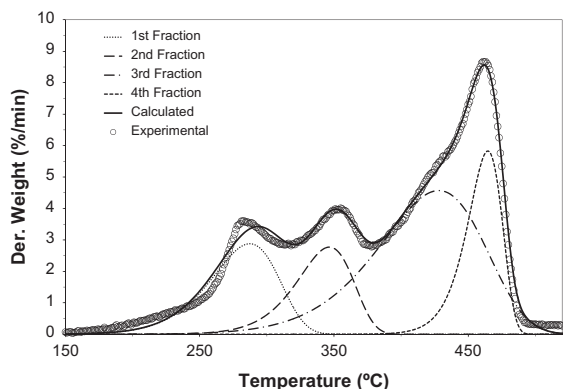
The pyrolysis behavior of the RDF is modeled by assuming four independent parallel first-order reactions. A MATLAB<sup>®</sup> code was written to simulate the devolatilization curves and to calculate the kinetic parameters by solving the optimization problem formulated earlier. The calculated kinetic parameters are listed in Table 4. Fig. 3 compares the predicted and measured DTG curves of the RDF samples, indicating that there is a good agreement between experiment and numerical model. It should be kept in mind that the four reactions used in the kinetic model are pseudoreactions which are the summative result of a large number of primary reactions with similar reactivities. Nevertheless, the behavior of the first two pseudocomponents or fractions (low temperature region) resembles the behavior of hemicellulose and cellulose, respectively. Comparative studies found in the literature [10,11,15] also include lignin as a pseudocomponent as it constitutes the third main component in lignocellulosic materials. However, given the fact that lignin decomposition does not show as a separate peak in the DTG profile, this curve does not contain any information that can be used to create a reaction for the lignin decomposition. Gronli had already noticed this in his early work related to wood decomposition [12], where he mentioned that only the flat tailing section at the descending part of the DTG curve contains information related to lignin decomposition. This formal approximation resulted in extremely low activation energies and corresponding frequency factors. RDF material contains plastics, thus the flat tailing section observed for lignocellulosic samples is not observed here, as it overlaps with the decomposition of the plastics fraction. For this reason, the 'cellulose' peak is believed to also cover lignin decomposition. The relatively broad peak observed for the cellulose component supports this assumption. A more elaborate discussion can be found at the end of this section.

At higher temperatures, the DTG curve shows a broad peak that is accurately described by the devolatilization kinetics for plastics. Grammelis et al. [10] investigated the thermal stability of different types of plastic material. Based on the conversion rate curves, the following order was found (stability decreases from left to right): PC > HDPE > LDPE > PP > PA > PS > PVC. As mentioned earlier, plastics found in waste streams arise from a variety of sources and thus the types of plastics vary accordingly. For this reason, two pseudocomponents are required to mimic the plastics devolatilization behavior observed experimentally. In Table 4, the third pseudocomponent groups the less stable plastics, the fourth pseudocomponent the thermally more stable plastics. In the last paragraph of this section, the *E* and *A* values presented in this paper are compared to the values found in the literature.

Fig. 3 shows that around 380 °C, the curves for lignocellulosic and plastics decomposition partially overlap. This phenomenon has not been observed in other studies describing RDF decomposition. A combination of factors could be responsible for this type of behavior: (a) industrial waste contains other types of material compared to household waste (*e.g.* reinforced plastics, flame retardant material), there has not yet been any research performed on RDF processed from industrial waste, (b) inorganic matter has a catalytic effect on the decomposition of lignocellulosic material, (c) metal oxides such as ferric oxide or Fe<sub>2</sub>O<sub>3</sub> (found in RDF ash) are known to catalyze the decomposition of plastics [24].

**Table 4**  
Calculated kinetic parameters for RDF pyrolysis, 4 pseudocomponents (heating rate 10 °C/min).

First fraction			Second fraction			Third fraction			Fourth fraction		
$E$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$c$ (wt%)	$E$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$c$ (wt%)	$E$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$c$ (wt%)	$E$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$c$ (wt%)
100	7.9E8	18.8	149	1.8E12	15.1	99	5.6E6	46.4	353	7.8E24	19.6



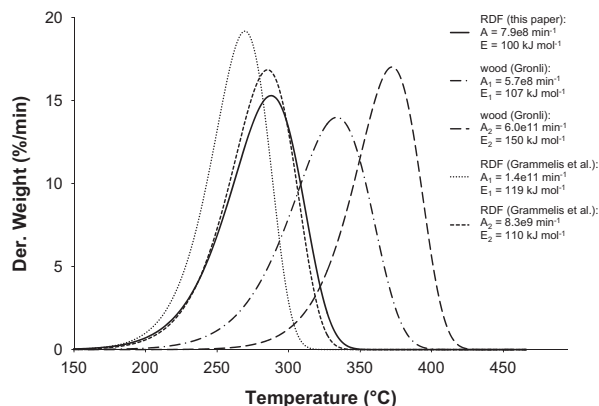
**Fig. 3.** Experimental and calculated DTG curve, 4 pseudocomponents (heating rate 10 °C/min).

It should be noted that there is no true quantitative relationship between the  $c_i$  values calculated and the actual mass fractions of hemicellulose, cellulose and plastics (denoted as  $w_i$ ) found in the RDF material. The parameters  $c_i$  express the contribution of the partial processes to the overall mass loss and thereby the *volatile* part of each component. The relationship between  $w_i$  and  $c_i$  is expressed by Eq. (7) [12].

$$\sum_i w_i = \sum_i c_i + m_{char} = \sum_i (m_{0,i} - m_{char,i}) + \sum_i m_{char,i} = 1 \quad (7)$$

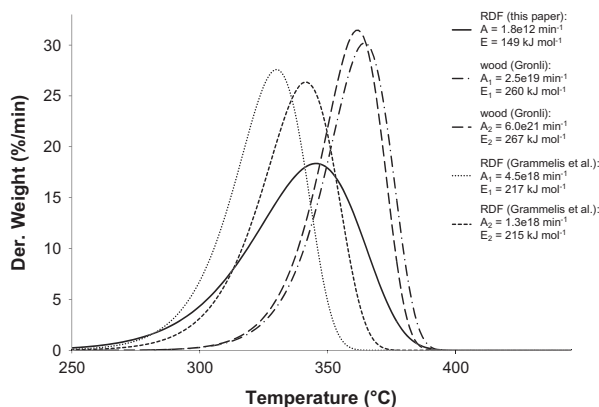
In order to establish a relationship between the calculated  $c_i$  values and the actual mass fractions  $w_i$ , the char fractions for the independently decomposing components,  $m_{char,i}$ , have to be known. However, these individual char fractions cannot be measured in practice. Hence, it can be concluded that this type of modeling cannot serve as a way to estimate the composition of the investigated material.

The literature provides a broad range of kinetic parameters for hemicellulose, cellulose, and plastics. These values depend on the material used (pure component or composite material) and on the specific pyrolysis conditions, i.e. temperature profile, heating rate, pressure, particle size, ambient gas environment, and the presence of ash or mineral matter. The first fraction of the examined RDF material closely resembles hemicellulose, with an activation energy of 100 kJ mol<sup>-1</sup> and a preexponential factor of 7.9E8 min<sup>-1</sup>. Both values fall within the range of data found in the literature. Grammelis has found an average activation energy of 117 kJ mol<sup>-1</sup> and a preexponential factor of 10.5E11 min<sup>-1</sup> for the hemicellulose fraction present in RDF material [10]. Gronli has investigated different types of wood, resulting in (hemicellulose) activation energies ranging from 92 to 144 kJ mol<sup>-1</sup>, and preexponential factors ranging from 2.5E7 to 4.8E12 min<sup>-1</sup> [12]. Fig. 4 compares the DTG curves that correspond to these different combinations of frequency factors and activation energies. Hemicellulose degradation in RDF (both fresh and aged waste material) takes place over a lower temperature range compared to hemicellulose found in wood. The catalytic effect of metals and/or inorganic matter (found in the RDF) could play a role here.



**Fig. 4.** Comparison of hemicellulose DTG curves: RDF (this paper), RDF from other sources [10], wood [12].

The calculated kinetic parameters for the second fraction of the examined RDF give the impression that the thermal degradation behavior does not correspond very well with the behavior of cellulose. For the second fraction of the RDF material, the activation energy and the preexponential factor equal 149 kJ mol<sup>-1</sup> and 1.8E12 min<sup>-1</sup>, respectively. In the literature, the average activation energy and preexponential factor reported for cellulose found in fresh RDF material are 217 kJ mol<sup>-1</sup> and 3.7E18 min<sup>-1</sup> [10]. The corresponding values found for cellulose in wood are 260 kJ mol<sup>-1</sup> and 2.5E19 min<sup>-1</sup> [12]. Fig. 5 compares the DTG curves that correspond to these different combinations of  $A$  and  $E$  values. All curves are close together, which means it is safe to assume that all these different combinations of kinetic parameters give a good representation of cellulose degradation. Even though the activation energies and frequency factors vary greatly, their combined effect is quite consistent. This is explained by the kinetic compensation effect, which consists of a correlation between the kinetic parameters [12]. The cellulose fraction found in RDF material (Grammelis et al. [10] and this study) exhibits a lower peak temperature compared to the cellulose fraction found in wood. This could be



**Fig. 5.** Comparison of cellulose DTG curves: RDF (this paper), RDF from other sources [10], wood [12].

explained by the catalytic effect of inorganic matter on the thermal degradation behavior, as mentioned earlier in this section. Furthermore, the peak that belongs to the RDF material studied here, is wider than the other peaks. This is confirmed by the low activation energy, as it is known that the activation energy (for a single first order reaction) is inversely proportional to the peak width [12]. The fact that lignin decomposes over a wide range of temperatures, overlapping with cellulose degradation, could give a possible explanation for this broader peak. As lignin decomposition cannot be attributed to a distinct peak, the 'cellulose' peak also covers lignin decomposition.

The third fraction displays a lower activation energy (i.e.  $99 \text{ kJ mol}^{-1}$ ) and preexponential factor (i.e.  $5.6\text{E}6 \text{ min}^{-1}$ ) than expected for plastics, as it also covers part of the temperature region in which lignocellulosic materials degrade. The fourth fraction on the other hand, does provide a good representation of plastics degradation, with an activation energy of  $353 \text{ kJ mol}^{-1}$  and preexponential factor of  $7.8\text{E}24 \text{ min}^{-1}$ . These results agree well with the findings of other researchers who reported activation energy values (averaged) of  $334 \text{ kJ mol}^{-1}$  for plastics in fresh RDF material, and  $378 \text{ kJ mol}^{-1}$  for pure plastics [10]. Similarly, the reported values for the preexponential factors are equal to  $3.4\text{E}23 \text{ min}^{-1}$  (fresh RDF) and  $5.9\text{E}29 \text{ min}^{-1}$  (pure plastics) [10].

#### 4. Conclusions

The results presented in this manuscript indicate that RDF is a very complex material as its composition and hence its pyrolysis characteristics can vary widely. This is especially true for excavated (i.e. aged) waste material of which the origin and/or composition is often not clearly defined.

The independent parallel first-order reactions model is used for the kinetic analysis of the thermal decomposition behavior. The degradation behavior of the RDF is described by four pseudocomponents. The model is found to provide a good fit to the measured data, as it is able to capture both the degradation of the lignocellulosic and the plastics fraction found in the waste material. The kinetic parameters found for the first pseudocomponent ( $E = 100 \text{ kJ mol}^{-1}$ ,  $A = 7.9\text{E}8 \text{ min}^{-1}$ ) agree well with the kinetic parameters for hemicellulose reported in the literature. The same applies to the second component, i.e. cellulose ( $E = 149 \text{ kJ mol}^{-1}$ ,  $A = 1.8\text{E}12 \text{ min}^{-1}$ ). The low activation energy found for cellulose results in a relatively broad peak. This is believed to be caused by the fact that lignin decomposition cannot be attributed to a distinct peak, but instead also contributes to the 'cellulose' peak.

Due to the partial overlapping of the curves describing cellulose and plastics degradation, the kinetic data for the third pseudocomponent ( $E = 99 \text{ kJ mol}^{-1}$ ,  $A = 5.6\text{E}6 \text{ min}^{-1}$ ) do not fully agree with the pure component kinetic data, which is assumed to cover the less stable plastics. The kinetic parameters belonging to the fourth pseudocomponent are similar to the literature values reported for (stable) plastics ( $E = 353 \text{ kJ mol}^{-1}$ ,  $A = 7.8\text{E}24 \text{ min}^{-1}$ ).

Thermogravimetric analysis is performed on the RDF samples, under strictly controlled conditions and at a low heating rate, resulting in (slow) pyrolysis chemical kinetics. The suggested approach, TGA combined with parameter estimation, can be regarded as a generic method to derive the kinetic parameters for the RDF material under investigation. The authors would advise researchers to perform TGA experiments on the RDF samples in order to get a clear picture of the degradation behavior. If the RDF is processed from household waste, its profile may closely match the profiles found in the literature. In that case, the kinetic parameters quoted there, are expected to provide a good approximation.

However, if the RDF is processed from more 'exotic' waste streams (e.g. industrial waste, excavated waste), its DTG profile is more likely to deviate from the profiles presented in the literature. In that case, a good estimation of the kinetic parameters can be found by following the generic method proposed in this paper, from start to finish (i.e. from TGA experiments up to parameter estimation). By coupling the obtained pyrolysis kinetics with heat and mass transfer, accurate simulation models for real-life thermochemical conversion systems can be obtained.

#### Acknowledgements

The authors would like to acknowledge the financial support through the IWT O&O project *Closing the Circle and Enhanced Landfill mining as part of the transition to Sustainable Materials Management*, and fruitful discussions with Group Machiels. Moreover, the post-doctoral fellowship of Christopher de Dobbelaere, funded by the Research Foundation – Flanders (FWO Vlaanderen) is acknowledged.

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