UNIVERSITY of York

This is a repository copy of *The combined effect of plastics and food waste accelerates the thermal decomposition of refuse-derived fuels and fuel blends*.

White Rose Research Online URL for this paper: <u>https://eprints.whiterose.ac.uk/149467/</u>

Version: Published Version

Article:

Edo, Mar, Budarin, Vitaliy, Aracil, Ignacio et al. (2 more authors) (2016) The combined effect of plastics and food waste accelerates the thermal decomposition of refuse-derived fuels and fuel blends. Fuel. pp. 424-432. ISSN 0016-2361

https://doi.org/10.1016/j.fuel.2016.04.062

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk https://eprints.whiterose.ac.uk/

Fuel 180 (2016) 424-432

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

The combined effect of plastics and food waste accelerates the thermal decomposition of refuse-derived fuels and fuel blends



COMBUSTIBLE FUEL FRACTION (FF)

FINE FRACTION

(organic matter and recyclable materials)

DRY NON-ORGANIC COMBUSTIBLE

FRACTION (EFF)

WET ORGANIC FRACTION

Mar Edo^{a,b}, Vitaliy Budarin^c, Ignacio Aracil^d, Per-Erik Persson^e, Stina Jansson^{a,*}

^a Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

^b Industrial Doctoral School, Umeå University, SE-901 87 Umeå, Sweden

^c Green Chemistry Center of Excellence, Department of Chemistry, University of York, Heslington, York Y010 5DD, UK

^d University Institute of Chemical Processes, University of Alicante, P.O. 99, Alicante, Spain

^e Vafabmiljö AB, SE-721 87 Västerås, Sweden

HIGHLIGHTS

GRAPHICAL ABSTRACT

- Shredding and screening reduces the chlorine content in MSW fuels by up to 64%.
- Recovered wood and virgin wood exhibited similar combustion behaviour and properties.
- Reactivity in fuels increased with the food waste content.
- A combination of plastics and food waste in a fuel matrix accelerates its decomposition.

A R T I C L E I N F O

Article history: Received 12 October 2015 Received in revised form 11 April 2016 Accepted 12 April 2016 Available online 20 April 2016

Keywords: Municipal solid waste (MSW) Thermochemical conversion Co-combustion DSC TG-FTIR

ABSTRACT

Mechanical treatments such as shredding or extrusion are applied to municipal solid wastes (MSW) to produce refuse-derived fuels (RDF). In this way, a waste fraction (mainly composed by food waste) is removed and the quality of the fuel is improved. In this research, simultaneous thermal analysis (STA) was used to investigate how different mechanical treatments applied to MSW influence the composition and combustion behaviour of fuel blends produced by combining MSW or RDF with wood in different ratios. Shredding and screening resulted in a more efficient mechanical treatment than extrusion to reduce the chlorine content in a fuel, which would improve its quality. This study revealed that when plastics and food waste are combined in the fuel matrix, the thermal decomposition of the fuels are accelerated. The combination of MSW or RDF and woody materials in a fuel blend has a positive impact on its decomposition.

SHREDDERING AND

SCREENING

EXTRUDER PRESS

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND licenses (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The impact of fossil fuels on the environment and human health has led to a search for alternative fuel sources able to replace fossil

fuels in terms of energy capacity, but also with a reduced environmental impact. In other words, our society is facing the challenge of finding new sustainable fuels, and biomass and waste materials are among those with the potential to replace fossil fuels.

Almost 1.9 billion tons of household waste also known as municipal solid waste (MSW) are generated globally every year, which means about 218 kg/person annually [1]. Of the MSW collected: 19% is recycled, 11% is used in energy recovery processes and the rest ends up in landfills or dumps [1]. Almost 4.5 Mtons of

^{*} Corresponding author.

E-mail addresses: mar.edo@umu.se (M. Edo), vitaliy.budarin@york.ac.uk (V. Budarin), nacho.aracil@ua.es (I. Aracil), per-erik.persson@vafabmiljo.se (P.-E. Persson), stina.jansson@umu.se (S. Jansson).

This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

MSW (460 kg/person annually) were produced in Sweden during 2013, of which 32% was recycled, 15% was used in biological treatment and 52% was sent for energy recovery [1,2]. MSW incineration significantly reduces the volume of the waste and sanitizes it. In addition, combining MSW incineration with energy recovery (Waste-to-Energy, WtE) is an effective method of waste disposal. However, the heterogeneity and high moisture content of MSW make pre-treatment necessary to enhance its properties as fuel. Shredding and sieving is widely used to convert MSW into a more efficient fuel by reducing its particle size, separating out materials that can be recycled, such as ferrous and non-ferrous metals, and reducing the amount of wet material, such as food waste, than can be used for other purposes. Another emerging mechanical treatment involves extrusion of MSW in a hydraulic press providing a dry waste fraction for combustion. This fraction is mainly composed by plastic, paper and cardboard. Both shredding and extrusion reduce the food waste content from the processed combustible fraction which is subsequently known as refuse-derived fuel (RDF).

Removing food waste from the MSW would probably result in higher quality RDF. In addition, food waste could be more efficiently used for the production of biogas and compost. Food waste, paper and plastics are the main source of chlorine in MSW [3,4]. Power plants operating with RDF have high corrosion rates in their boilers due to the presence of chlorine in the fuel, which increases the maintenance costs of the plants. In addition, chlorine is responsible for the formation of toxic chlorinated pollutants such as dioxins and furans [5].

On the other hand, biomass has become one of the most indemand renewable energy sources in recent years since it is considered to be carbon-neutral. Woody biomass generally has low ash content, a high concentration of volatiles [6] and higher energy content compared to MSW [7]. Other woody materials, such as recovered wood from demolition and construction activities, are also being used in WtE processes but they have not been as extensively studied as other types of biomass.

Production of fuel blends by combining woody materials and MSW has great potential with regard to both environmental and economic benefits compared to MSW-only fuels. The total chlorine content (TCC) of the fuel would be lower, which may reduce the risks of corrosion problems in the boilers and potential emissions of chlorinated organic compounds to the air. In addition, combustion behaviour and energy content of the fuel blend could be improved resulting in more efficient combustion. There is a lack of knowledge about how mechanical treatments applied to MSW influence its composition and properties and, by extension, its co-combustion behaviour, when combined with wood for the production of fuel blends.

Thermal analysis (TA) is a reliable technique used extensively for simulating thermal processes since it readily provides information about the thermal decomposition and combustion behaviour of a fuel. TA has been used extensively for the study of the cocombustion of biomass and coal or lignin blends [8–14] and even MSW and coal blends [15]. However, there are few studies considering the co-combustion of woody materials and MSW or RDFs. Grammelis et al. [16] focused on pyrolysis and combustion characteristics of the components of RDFs, while Muthuraman et al. [15,17] compared co-combustion characteristics of coal with MSW treated hydrothermally and wood. Synergies between RDF and biomass in a fixed-bed reactor were studied by Gehrmann et al. [18].

The current work used simultaneous thermal analysis (STA) to examine the combustion behaviour of different fuel materials and their blends. Two different types of woody materials (virgin softwood pellets and recovered wood chips) and three different waste materials (one MSW as collected and two RDFs obtained by mechanical treatment) were combined in two different fuel blend ratios. The aim of this study was to investigate how two different mechanical treatments applied to MSW influence the composition and combustion behaviour of the RDF. It also examines how the combustion behaviour of different fuel blends is influenced by the fuel matrix and the fuel blend ratios. Finally, the differences when recovered wood is used instead of virgin softwood were investigated. The results obtained will provide useful information for the production of fuel blends.

2. Materials and methods

2.1. Individual fuels and their preparation

Five different fuel materials were tested and used for the production of fuel blends – two woody materials, one MSW and two RDFs:

- 1. *Virgin wood pellets* (WP). Commercial softwood pellets (mix of pine and spruce) used for domestic heating.
- 2. *Recovered wood chips* (RW) from industrial, construction and demolition activities.
- 3. *Municipal Solid Waste remains* (MSWr). This is the remaining fraction after food waste has been collected separately from MSW on an individual basis in households. It mainly comprises plastics, paper, cardboard, textiles and food waste, and it may contain 5–20 wt.% food waste, depending on the efficiency of the separation of food waste in the source households.
- 4. *Fuel Fraction* (FF). By shredding and screening the MSWr in a grinder (Doppstadt DW 3060) and a 100 mm drum-screen (Doppstadt SM 518) two fractions are obtained: a fine fraction and a coarse (fuel) fraction. The fine fraction contains mainly incombustible materials and food waste, which can be used in compositing or anaerobic digestion processes. The fuel fraction (FF) is a RDF suitable for combustion. It mainly contains plastic and paper compounds and may contain up to 5 wt.% food waste due to inefficiencies in the screening process.
- 5. *Extruder Fuel Fraction* (EFF). By compressing MSWr in an extruder hydraulic press (*VM Press*[®]) the waste is separated into two fractions: a wet fraction mainly comprising food waste suitable for biological processes and a dry fraction rich in combustible materials such as paper, plastic or cardboard. The dry combustible fraction, also considered to be a RDF, may contain up to 2% food waste. Hereafter, it will be referred to as the extruder fuel fraction (EFF).

All fuels except WP were collected from a recycling centre and waste treatment plant sited in southern Sweden and owned by VafabMiljö AB. For each individual fuel, a standardized quartering procedure was performed to ensure a 25 kg representative sample of each type. Since the amount of sample used in the tests was very low, it was important to perform thorough grinding and homogenization to ensure representative and homogenous samples for analysis. Prior to analysis, samples were air dried and metal and glass pieces were removed manually from the waste materials and RW. Next, samples were homogenized, ground using a Retsch SM 200 cutting mill and sieved to ≤ 1 mm and homogenized again. Finally, materials were ground again and sieved to $\leq 500 \,\mu\text{m}$ and further homogenized prior to analysis (see Figs. S1–S3 available in supplementary material about FF and EFF production and sampling and sample preparation respectively).

2.2. Fuel blend preparation

Fuel blends were prepared by combining all the individual fuels in two different waste:wood ratios: (i) 80:20 and (ii) 60:40 by weight. The first ratio (80:20) is widely used in fuel blends for cocombustion; while the second one (60:40) is an attempt to produce a fuel blend with enhanced properties in terms of energy and pollutants released. In total, 12 fuel blends were obtained by blending each woody material with either MSWr or one of the RDFs, in the two blend ratios.

2.3. Sample characterization

Elemental analysis (CHN) was performed according to the EN15407:2011 standard [19]. Sulphur and chlorine determinations were performed according to the EN 15408:2011 standard [20]. Oxygen content was calculated by difference. These analyses were performed by Bränslelaboratoriet Umeå AB. Energy content was determined using a LECO AC-350 bomb calorimeter on 0.5 g of dry sample. Proximate analysis was carried out in a STA 6000 Per-kin Elmer Thermobalance using 5–15 mg of sample and 70 mL min⁻¹ gas flow [21]. The decomposition of the fuels under pyrolytic conditions with Fourier transform infrared spectroscopy (TG-FTIR) was performed using a thermogravimetric analysis coupled Netzsch STA 409 at a heating rate of 10 °C min⁻¹, with typically 30 mg sample under flowing N₂ at 100 mL min⁻¹, coupled with a Bruker EQUINOX-55 instrument equipped with a liquid N₂ cooled MCT detector.

2.4. Combustion studies in the STA

Combustion tests were performed in a Thermal Analyser (STA Stanton - Redcroft 625) which allows simultaneous Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). For each run, 2-4 mg of dried sample was placed in an Al₂O₃ pan and heated at 10 °C min⁻¹ from room temperature up to 600 °C in an oxygen atmosphere with a flow rate of 60 mL min⁻¹. The instrument was regularly calibrated according to IUPAC procedure [22]. Temperature measurement is granted within 0.1% and heat flow within 2%. Therefore, the position of the peaks reported in the paper has been measured very accurately. The peak positions are determined not only by the physical property of a fuel but also by experimental parameters such as the sample mass, the particle-heating rate, and the condition of surrounding gases. The sample weight loss, temperature, heat flux and time data were recorded simultaneously during the tests and used for the production of the TG, DTG (1st derivative of the TG curve) and DSC combustion curves, which represent weight loss of the sample, rate of weight loss and heat flux, respectively, as functions of temperature. Initial temperature (T_i, T_i) "temperature where the rate of weight loss accelerates due to the onset of the combustion") [23] and *burnout temperature* were obtained graphically based on the intersection point between the base line and the tangent to the maximum slope in the first peak and in the last peak of the DSC curve respectively.

Elemental analysis, sulphur and chorine determination were performed for the individual fuels, while calorific values, proximate analysis and thermogravimetric analysis were performed for all individual fuels and blends. All the experiments were replicated at least three times to ensure reproducibility of the results.

3. Results and discussions

3.1. Individual fuels

3.1.1. Physical and chemical properties

The physical and chemical properties of both wood materials studied, WP and RW, were very similar (Table 1). Volatiles and oxygen content are indicators of how easy is to ignite a fuel [17]. Results showed that woody materials have higher volatile content than MSW-based fuels (85.6% and 72–80% respectively); as well as much higher oxygen content (40–41% and 24–25.5% respectively). Comparison of MSW-based fuels showed that FF has the highest volatile matter (79.6%) followed by EFF and MSWr (72.9% and 72.0% respectively) and very similar oxygen contents (about 24.7%). The ash content was vastly lower in woody fuels (2%) compared to MSW-based fuels (17–23.6%). As the nitrogen (0.10–1.10%) and sulphur content (0.01–0.15%) was low in all the fuels, low SO_X and NOx emissions could be expected when these materials were used as fuels in combustion or co-combustion processes.

Chlorine content was substantially lower in woody (<0.01%) than in MSW-based fuels (0.3–0.9%) due mainly to the presence of food waste and traces of chlorinated plastics in the latter [3–5]. A comparison of the levels of chlorine in MSWr and RDFs showed that both mechanical treatments, shredding and screening and extrusion, applied to the MSWr decrease the chlorine content in the source from 0.89% to 0.32% and 0.50% respectively by removing food waste. Based on these results, shredding and screening is a more efficient method for removing chlorine from fuel than extrusion.

All the fuels tested, except FF (22 MJ/kg_{db}), had similar energy contents $(17-19 MJ/kg_{db})$, which can be considered an advantage when MSWs are blended with woody materials. Even when the materials are not homogenously blended, there would not be big variations in heat released.

By decreasing the food waste content in MSWr it is possible to obtain a fuel with enhanced energy content. Based on the individual fuel properties, FF is the one with the most improved properties.

3.1.2. Fuel decomposition under pyrolytic conditions: TG-FTIR in WP and EFF

TG-FTIR was used to examine the decomposition of the fuels under pyrolytic conditions. This technique provides information about the volatiles evolved during the decomposition of the fuels as well as the temperature ranges involved. TG-FTIR analysis was conducted on two of the materials, WP and EFF. The TG-FTIR spectra of the pyrolysis of WP show one-step decomposition (Fig. 1A1 and A3), which demonstrates the homogeneity of this material. The first volatiles from the WP decomposition appeared after 250 °C and were released slowly. At this stage carbon

Table	1
-------	---

Individual fuel characterization.

Sample	Proximate analysis (% _{db})		Ultimate analysis (% _{db})					Energy content (MJ/kg _{db})		
	Volatile matter	Fixed carbon	Ash	С	Н	Ν	S	0	Cl	LHV ^a
WP	85.5	12.1	2.4	51.2	6.2	0.1	0.03	40.1	<0.01	18.0
RW	85.7	12.3	2.0	50.4	6.2	0.4	0.01	41.0	< 0.01	17.9
MSWr	72.0	4.4	23.6	43.9	6.1	1.1	0.15	24.3	0.89	17.2
FF	79.6	3.3	17.2	50.4	7.2	0.4	0.10	24.4	0.32	21.9
EFF	72.9	4.4	22.7	44.6	6.3	0.4	0.08	25.4	0.50	19.3

db: dry basis.

^a LHV: lower heating value.

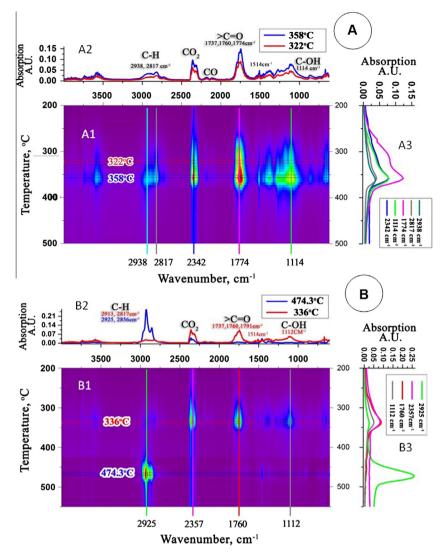


Fig. 1. TG-FTIR analysis of (A) softwood pellets (WP) and (B) extruder fuel fraction (EFF). A1 and B1: two dimensional representation of the pyrolysis. A2 and B2: FTIR spectra of volatiles produced at 322 °C and 336 °C and 336 °C and 474 °C, respectively. A3 and B3: kinetic traces of the major FTIR absorption peaks (A.U.: Absorbance units).

dioxide as well as ketones, aldehydes and carboxylic acids dominated. The carboxylic acids and especially the ketones and aldehydes are highly flammable and could be easily ignited by heat initiating combustion of the WP. The maximum organic volatile release was observed at a temperature around 360 °C (with a lower threshold around 320 °C). It is important to note that at 360 °C, in contrast to the lower temperature boundary, a significant quantity of high calorific value aliphatic compounds (peaks ca. 2820 and 2930 cm⁻¹) was observed. Large quantities of aliphatic compounds such as CH₄ are produced from lignin decomposition [24].

TG-FTIR spectra obtained during the pyrolysis of EFF (Fig. 1B1 and B3) demonstrate the heterogeneous nature of this sample with two well separated peaks at 336 °C and 474 °C. The first peak is associated with release of carbon dioxide, aldehydes, ketones and acids. The composition of volatiles produced from EFF at 336 °C is similar to the main peak of the WP decomposition and is probably the result of decomposition of bio-derived polymers. In contrast, the major products of decomposition at 474 °C are long chain aliphatic compounds (corresponding to the peaks at 2925 and 2826 cm⁻¹). This stage of the EFF decomposition could be associated with synthetic polymers that may produce substantial amounts of flammable high calorific value compounds during decomposition.

3.1.3. Combustion behaviour

Individual fuels were tested by STA to study their combustion behaviour and to elucidate how each fuel differs from the others when they are burnt. The thermal oxidation of RW and WP revealed very similar combustion behaviours occurring in two stages (Fig. 2A). According to TG-FTIR data (Fig. 1A) the first stage (ca. 350 °C) is attributed to the oxidation of volatiles produced during the total decomposition of cellulose, hemicellulose and partial decomposition of lignin [8,25,26]. During this stage, most of the volatiles are oxidized and char is formed. The second stage (ca. 470 °C) is attributed to the decomposition and oxidation of the remaining lignin and the char created during the first stage [8,25]. The main loss of weight occurred during the first stage: 62.2% and 58.9% for RW and WP respectively. From 350 °C upwards, both materials had the same loss of weight (ca. 60%) and ash content (ca. 4%). The two wood-based fuels' DSC profiles (Fig. 2B) showed two exothermic peaks which correspond to the decomposition stages observed in the TG profiles. Based on these results we can say that RW and WP exhibit similar combustion behaviour

MSW-based fuels exhibited three-stage oxidation. Compared to WP and RW, an early third peak appeared while the other two peaks shifted to lower temperatures, which can be easily observed in FF and EFF (Fig. 2D). The temperature ranges for each

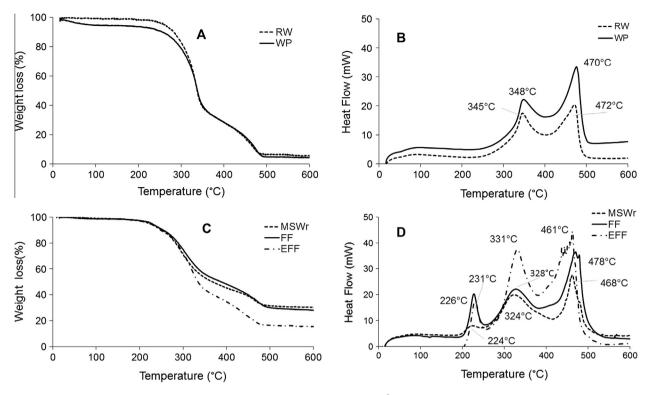


Fig. 2. TG (A and C) and DSC (B and D) profiles of the combustion of the individual fuels at 10 °C min⁻¹: RW (recovered wood); WP (softwood pellets); MSWr (municipal solid waste remains); FF (fuel fraction) and EFF (extruder fuel fraction).

decomposition stage were 200-260 °C; 260-375 °C and 375-500 °C respectively. The nature of each peak could be interpreted based on TG-FTIR analysis of EFF (Fig. 1B). The EFF decomposition consists of two peaks at 336 °C and 474 °C that correspond to the pyrolysis of two types of components: lignocellulosic material (food, paper, cardboard and wood) and synthetic polymers, respectively. Therefore, the two major combustion peaks of EFF at 331 °C and 461 °C (Fig. 2D) could be attributed to oxidation of volatiles produced during the pyrolysis of lignocellulosic and synthetic polymers present in the sample. However, the complexity and broadness of the 461 °C peak (Fig. 2D) could be attributed to the oxidation of the char obtained during pyrolysis of lignocellulosic materials at 331 °C. The first combustion peak around 225 °C in the MSW-based fuels was associated with very little sample mass loss in STA (Fig. 2D). Surprisingly, this peak does not exist in TG trace of TG-FTIR experiment (see Fig. 1B). However, FTIR analysis of volatiles produced at temperature around 225 °C demonstrates some quantity of carbonyl (C=0) and carboxyl (C-OH) containing molecules. Therefore, the nature of the 225 °C peak in the MSW oxidation STA trace could be attributed to oxidation of the carbonyl and carboxyl containing volatiles molecules released from plastics.

DSC profiles (Fig. 2D) showed that the first peak was more intense when the amount of non-lignocellulosic materials in the fuel increased, in other words, when the food waste content decreased. This fact supports our theory that the first peak is due to the decomposition of non-lignocellulosic materials such as plastics or easily decomposed components. At the same time, it can be clearly seen in the DSC profiles that when the food waste content in a fuel increased, the second peak shifted to lower temperatures. Based on these observations, it seems that the presence of food waste also accelerates the decomposition of the fuels, which is also indicated by the initial temperature in Table 2.

MSW-based fuels have a lower *initial temperature* than woody fuels, 203–210 °C and 287 °C respectively and MSWr and FF have the highest burnout temperatures, about 501 °C, due to their high

Table 2

Initial temperature	(T_i) and	burnout (T_{bo}) temperature	for the	individual fuels	•
---------------------	-------------	--------------------	---------------	---------	------------------	---

Sample	Blend ratio	T_i (°C)	$T_{\rm bo}$ (°C)	
WP	100	287	495	
RW	100	287	487	
MSWr	100	203	501	
FF	100	205	502	
EFF	100	210	485	
MSWr:RW	60:40	200	491	
MSWr:RW	80:20	200	508	
FF:RW	60:40	220	495	
FF:RW	80:20	210	490	
EFF:RW	60:40	216	491	
EFF:RW	80:20	216	500	

ash content (Fig. 2C) [26]. The acceleration on the thermal decomposition of the fuels due to the presence of plastics in the MSWbased fuels could explain the fact that MSWs-based fuels have lower initial temperature than wood-based fuels although their volatile matter and oxygen content is lower (see Section 3.1.1). On the other hand, results showed that the higher the amount of food waste in a fuel, the lower the initial temperature is. Based on these results, if plastics were the only component responsible for shifting the MSW-based fuels' curves to lower temperatures, then those fuels with a higher plastic content would have the lower T_i . However, the fuel with the lower T_i is the one with higher food waste content. For this reason, we consider that instead of an effect due solely to the plastics, the acceleration of the decomposition of the waste could be due to a combined effect of the food waste and plastics present in the fuel.

Previous studies in this field have reported an acceleration in the thermal decomposition of some materials due to the presence of either PVC [16,27] or impurities that are easy to decompose [28]. However, this is the first study that provides clear observations of the three-stage oxidation of MSW-based fuels and in which food

waste is also considered to play an important role in combination with the presence of plastics. Due to the vast number of policies regarding restriction of the use of PVC (the use of PVC in consumer goods has been banned in Sweden since 1995) it is unlikely that the PVC content in waste is the same today as reported in previous studies [29]. For this reason, we conclude that PVC is not the only material responsible for the acceleration of the decomposition observed in our test, but it acts in combination with other plastic and non-woody combustible materials and food waste

Comparison of TG-curves of two different fuel materials (MSWr and FF) and two fuel blends (FF:WP and MSWr:WP, 80:20) and DSC curves of MSW-only fuels (MSWr and FF) and their replicates are shown in Figs. S7 and S8 respectively in supplementary material. These plots show that results from replicate are very reproducible.

3.2. Fuel blends

3.2.1. Physical and chemical properties

The results relating to the proximate analysis and energy content of the fuel blends were very similar when either WP or RW was used for the production of the blends (Table 3). The 60:40 waste:biomass blends were associated with lower ash content than the 80:20 blends. Furthermore, 80:20 fuel blends had higher

Table 3

Fuel blend characterization.

Sample		Proxima	ite analysis	Energy content (MJ/kg _{db})	
Waste:biomass	Blend ratio	Volatile matter	Fixed carbon	Ash	LHV ^a
MSWr:WP	60:40	78.9	8.7	12.4	18.0
MSWr:WP	80:20	73.7	5.9	20.4	17.4
MSWr:RW	60:40	77.0	9.6	13.4	18.0
MSWr:RW	80:20	74.4	8.1	17.5	17.4
FF:WP	60:40	79.4	5.4	15.3	20.4
FF:WP	80:20	79.0	3.9	17.1	20.9
FF:RW	60:40	78.0	9.3	12.7	20.1
FF:RW	80:20	79.2	4.3	16.5	20.8
EFF:WP	60:40	80.9	4.2	14.9	18.6
EFF:WP	80:20	76.3	2.0	21.7	19.1
EFF:RW	60:40	80.0	1.7	18.2	18.3
EFF:RW	80:20	81.1	3.2	15.8	18.7

db: dry basis.

^a LHV: lower heating value.

energy content, with the exception of those containing MSWr, since the energy content in MSWr and biomass fuels is quite similar. The fuel blends with the higher energy content were those containing FF (ca. 20.6 MJ/kg_{db}). Although FF is the MSW-based fuel with higher amounts of volatile matter, those blends containing EFF had the highest volatile matter content. In general, when biomass is added to MSW-based fuels, the volatile content of the fuel increases, the ash content decreases and the energy content remains almost the same with respect to MSW-based fuels. Based on the results of the characterization of the individual fuels and their blends, the addition of biomass to a MSW-based fuel enhances fuel quality.

Regarding the predictability of the fuel blends properties based on their individual fuels, a weighted law is verified both for energy content and volatile matter with differences between experimental and calculated values lower than 3% and 5% respectively. These differences become higher in fixed carbon and ash content determination, especially for those fuel blends with EFF, which can be attributed to the small amount of sample used to perform the proximate analysis experiments and the heterogeneity of the material.

3.2.2. Thermal properties: TG-FTIR in EFF-WP blend

TG-FTIR was applied to the fuel blend EEF:WP (80:20) to study the compounds evolved during its decomposition under pyrolytic conditions. DTG profiles of the EEF:WP blend and their individual components were also compared for a better understanding of the decomposition mechanism of these fuels. As can be clearly observed in the DTG profile (Fig. 3A), the decomposition of the EFF:WP fuel blend resulted in two-stages. The DTG curve of the blend is located between the DTG curves for the individual fuels, as could be expected. The second decomposition peak (474 °C) is due to the presence of EFF in the fuel blend, and its thermal behaviour is not affected by the presence of WP in the blend.

The DTG profile for the EFF:WP fits well with the FTIR spectra (Fig. 3B). Once again, the two-stage decomposition of the fuel blend (1st peak at 349.4 °C and 2nd peak at 474.3 °C) was observed. Analysis of volatiles produced during the pyrolysis of this fuel blend (Fig. 3B2 and B3) demonstrates some deviation in acid/aldehyde composition from the gas product composition obtained during the pyrolysis of the individual fuels. In addition, CO_2 (1760 cm⁻¹) is mainly released during the first stage

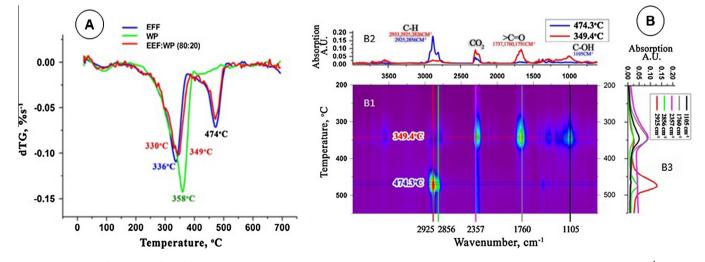


Fig. 3. A: Comparison of the DTG profiles of the individual EEF (extruder fuel fraction) and WP (wood pellets) fuels and their blends. Heating rate was 10 °C min⁻¹ and sample mass 30 mg, under pyrolytic conditions. TG-FTIR analysis of the EFF: WP 80:20 blend (B). B1: Two-dimensional representation of the pyrolysis. B2: FTIR spectrum of volatiles produced at 336 °C and 474 °C. B3: kinetic traces of the major FTIR absorption peaks (A.U.: Absorbance units).

decomposition, but a small and continuous release is also observed during the second stage.

3.2.3. Combustion behaviour

As has been mentioned in previous sections, WP and RW showed similar results in the proximate and ultimate analysis, with respect to energy content and combustion behaviour. Therefore, only the RW fuel blends were included in the evaluation of combustion behaviour. TG and DSC profiles for the individual fuels and their blends are presented in Figs. 4–6 (WP fuel blend profiles are available in Supporting information, Figs. S4–S6.).

The DSC curves for the fuel blends were located between the DSC curves of the individual fuels, as expected. The fuel blends presented three-stage oxidation as did the MSW-based fuels. Peaks were broader in the 80:20 blends than the 60:40 blends. The first small peak was more perceptible in the 80:20 than in the 60:40 blends, again supporting the idea of being related to the decomposition of synthetic polymers. The acceleration of the decomposition due to the presence of plastics and food waste discussed in Section 3.1.3 is also apparent in the fuel blends. The addition of RW shifted the second decomposition peak to a slightly higher temperature. As an example, in EFF:RW blends it shifted from 331 °C in

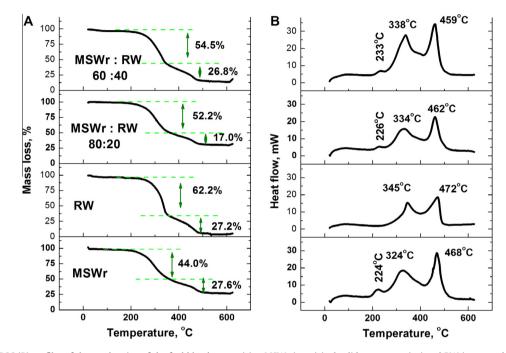


Fig. 4. TG (A) and DSC (B) profiles of the combustion of the fuel blends comprising MSWr (municipal solid waste remains) and RW (recovered wood) at 10 °C min⁻¹.

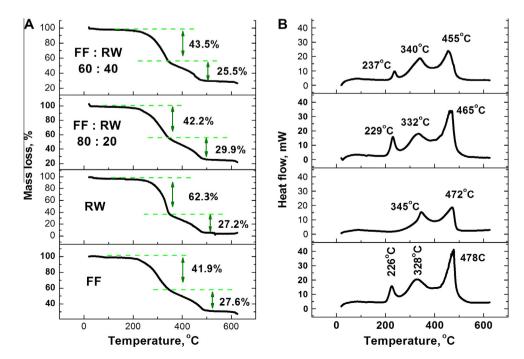


Fig. 5. TG (A) and DSC (B) profiles of the combustion of the fuel blends comprising FF (fuel fraction) and RW (recovered wood) at 10 °C min⁻¹.

454°C Α В 342°C 40 100 30 75 57.1% EFF:RW **5**39° 20 50 60:40 10 25 31.1% 0 0 40 100 338°C 455°C 30 236°C 75 47.9% EFF:RW Heat flow, mW 20 % 50 22.8% 80:20 10 Mass loss, 25 0 0 40 100 461°C 30 75 51.4% EFF 20 50 33 10 32.3% 25 0 0 40 100 30 75 472°C 62.2% RW 345°C 20 50 10 25 27.2% 0 0 200 400 600 200 400 600 °C Temperature, Temperature. °C

Fig. 6. TG (A) and DSC (B) profiles of the combustion of the fuel blends comprising EFF (extruder fuel fraction) and RW (recovered wood) at 10 °C min⁻¹.

the individual fuel to 338 °C and 342 °C in the 80:20 and 60:40 blends, respectively. Conversely, the third peak shifted to lower temperatures when the biomass in the blend increased: from 461 °C in the individual fuel to 455 °C and 454 °C in the 80:20 and 60:40 blends, respectively.

Initial temperature was slightly affected by the fuel ratio (Table 2). It was found that the higher the amount of food waste in a fuel blend, the lower the initial temperature (Table 2). The addition of biomass to MSW-based fuels slightly increased the initial temperature of fuel blends containing FF and EFF, and decreased the burnout temperatures by a few degrees in the FF blends but not in the MSWr and EFF blends. The acceleration of the thermal decomposition of the fuels due to the presence of non-cellulosic materials, such as plastics, and food waste is clearly observed again in the fuel blends.

4. Conclusions

Shredding and screening is a more efficient method for removing chlorine from fuel than extrusion. WP and RW have similar combustion behaviours and properties. Reactivity in fuels increases with the food waste content and it is slightly affected by the fuel blend ratio in combined fuels. For the first time, this study shows the three-stage oxidation in MSW-based fuels. When MSW/RDF and woody materials are combined for the production of fuel blends, the thermal decomposition of the fuel accelerates taking place at lower temperatures. This effect can be attributed to a combined effect of synthetic polymers and food waste present in the fuel matrix.

Acknowledgments

The authors would like to acknowledge Bio4Energy, a strategic research environment created by the Swedish government, for supporting this work. Junko Takahashi from Umeå Plant Science Centre (UPSC), Gunnar Kalen from the Swedish University of Agricultural Science (SLU) and Mirva Niinipuu (UmU) are acknowledged for their assistance with the sample preparation. Melissa Martinez and Carl-Magnus Pettersson for their assistance with the tests performed at Vafabmiljö.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2016.04.062.

References

- [1] D-Waste, Waste Atlas; 2013. <http://www.atlas.d-waste.com/>.
- [2] Avfall Sverige, Swedish Waste Management. Avfall Sverige (Swedish Waste Management); 2013.
- [3] Ma W, Hoffmann G, Schirmer M, Chen G, Rotter VS. Chlorine characterization and thermal behavior in MSW and RDF. J Hazard Mater 2010;178:489–98.
- [4] Themelis NJ. Chloride sources, sinks, and impacts in Waste-to-Energy power plants. In: 18th Annual North America waste-to-energy conference, Orlando, Florida, USA.
- [5] Svensson Myrin E, Persson P-E, Jansson S. The influence of food waste on dioxin formation during incineration of refuse-derived fuels. Fuel 2014;132:165–9.
- [6] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. Fuel 2010;89:913–33.
- [7] ECN, Phyllis2, database for biomass and waste. Energy Center of the Netherlands; 2015.
- [8] Vamvuka D, Sfakiotakis S. Combustion behaviour of biomass fuels and their blends with lignite. Thermochim Acta 2011;526:192–9.
- [9] Zhou C, Liu G, Fang T, Lam PKS. Investigation on thermal and trace element characteristics during co-combustion biomass with coal gangue. Bioresour Technol 2015;175:454–62.
- [10] Toptas A, Yildirim Y, Duman G, Yanik J. Combustion behavior of different kinds of torrefied biomass and their blends with lignite. Bioresour Technol 2015;177:328–36.
- [11] Sarkar P, Sahu SG, Mukherjee A, Kumar M, Adak AK, Chakraborty N, et al. Cocombustion studies for potential application of sawdust or its low temperature char as co-fuel with coal. Appl Therm Eng 2014;63:616–23.
- [12] Ohm TI, Chae JS, Kim JK, Oh SC. Study on the characteristics of biomass for cocombustion in coal power plant. J Mater Cycles Waste Manage 2014;17:249–57.
- [13] Zhou C, Liu G, Cheng S, Fang T, Lam PKS. Thermochemical and trace element behavior of coal gangue, agricultural biomass and their blends during cocombustion. Bioresour Technol 2014;166:243–51.
- [14] Varol M, Atimtay AT, Bay B, Olgun H. Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis. Thermochim Acta 2010;510:195–201.
- [15] Muthuraman M, Namioka T, Yoshikawa K. A comparative study on cocombustion performance of municipal solid waste and Indonesian coal with high ash Indian coal: a thermogravimetric analysis. Fuel Process Technol 2010;91:550–8.

- [16] Grammelis P, Basinas P, Malliopoulou A, Sakellaropoulos G. Pyrolysis kinetics and combustion characteristics of waste recovered fuels. Fuel 2009;88:195–205.
- [17] Muthuraman M, Namioka T, Yoshikawa K. A comparison of co-combustion characteristics of coal with wood and hydrothermally treated municipal solid waste. Bioresour Technol 2010;101:2477–82.
- [18] Gehrmann H-J, Kolb T, Seifert H, Mark F, Frankenhaeuser M, Schanssema A, et al. Synergies between biomass and solid recovered fuel in energy conversion processes. Environ Eng Sci 2010;27:557–67.
- [19] CEN, EN-15407:2011. Solid recovered fuels methods for the determination of carbon (C), hydrogen (H) and nitrogen (N) content. European Committee for Standardization; 2011.
- [20] CEN, EN-15408:2011. Solid recovered fuels. Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content; 2011.
- [21] Cassel B, Menard K. Proximate analysis of coal and coke using the STA 8000 Simultaneous Thermal Analyzer, PerkinElmer Application Note; 2012.
- [22] Gmelin E, Sarge St M. Pure Appl Chem 1995;67(11):1789–800.

- [23] Fan YS, Zou Z, Cao Z, Xu Y, Jiang X. Ignition characteristics of pulverized coal under high oxygen concentrations. Energy Fuels 2008;22:892–7.
- [24] Biagini E, Barontini F, Tognotti L. Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. Ind Eng Chem Res 2006;45:4486–93.
- [25] Skreiberg A, Skreiberg Ø, Sandquist J, Sørum L. TGA and macro-TGA characterisation of biomass fuels and fuel mixtures. Fuel 2011;90:2182–97.
- [26] Kok MV, Özgür E. Thermal analysis and kinetics of biomass samples. Fuel Process Technol 2013;106:739-43.
- [27] Sørum L, Grønli MG, Hustad JE. Pyrolysis characteristics and kinetics of municipal solid wastes. Fuel 2001;80:1217–27.
- [28] Vamvuka D, Sfakiotakis S, Saxioni S. Evaluation of urban wastes as promising co-fuels for energy production a TG/MS study. Fuel 2015;147:170–83.
 [29] Bernard J, Ole H, Vehlow J. The influence of PVC on the quantity and
- [29] Bernard J, Ole H, Vehlow J. The influence of PVC on the quantity and hazardousness of flue gas cleaning residues from incineration. European Commission; 2000.