Mixed fuels composed of household waste and waste wood
Characterization, combustion behaviour and potential emissions

Mar Edo Giménez
A mis padres

“El que no inventa no vive”

Ana María Matute
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>SECTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABLE OF CONTENTS</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>SAMMANFATTNING</td>
<td>iv</td>
</tr>
<tr>
<td>ABBREVIATIONS &amp; DEFINITIONS</td>
<td>v</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>v</td>
</tr>
<tr>
<td>Definitions</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF PUBLICATIONS</td>
<td>ix</td>
</tr>
<tr>
<td>Author’s contributions</td>
<td>x</td>
</tr>
<tr>
<td>1. THE IMPORTANCE OF WASTE IN TODAY’S SOCIETY</td>
<td>1</td>
</tr>
<tr>
<td>Converting waste to fuel</td>
<td>2</td>
</tr>
<tr>
<td>Waste Incineration</td>
<td>3</td>
</tr>
<tr>
<td>Drawbacks of incineration</td>
<td>4</td>
</tr>
<tr>
<td>Aims of this thesis</td>
<td>5</td>
</tr>
<tr>
<td>2. CONTAMINANTS &amp; POLLUTANTS</td>
<td>7</td>
</tr>
<tr>
<td>Contaminants</td>
<td>7</td>
</tr>
<tr>
<td>Pollutants</td>
<td>8</td>
</tr>
<tr>
<td>PCDDs and PCDFs</td>
<td>8</td>
</tr>
<tr>
<td>Related compounds</td>
<td>9</td>
</tr>
<tr>
<td>Toxicity</td>
<td>11</td>
</tr>
<tr>
<td>3. THE IMPORTANCE OF WASTE COMPOSITION</td>
<td>15</td>
</tr>
<tr>
<td>Variation in MSW composition</td>
<td>15</td>
</tr>
<tr>
<td>Importance of food waste in MSW</td>
<td>16</td>
</tr>
<tr>
<td>Variation in waste wood (WW) composition</td>
<td>17</td>
</tr>
<tr>
<td>4. UPGRADING WASTE TO FUEL</td>
<td>25</td>
</tr>
<tr>
<td>Waste Sources</td>
<td>26</td>
</tr>
<tr>
<td>Waste Wood</td>
<td>26</td>
</tr>
<tr>
<td>Household waste</td>
<td>27</td>
</tr>
<tr>
<td>From waste to fuel</td>
<td>28</td>
</tr>
<tr>
<td>Mechanical treatments</td>
<td>29</td>
</tr>
<tr>
<td>Mechanical Heat Treatment</td>
<td>32</td>
</tr>
<tr>
<td>Sampling and preparation of fuel blends</td>
<td>33</td>
</tr>
</tbody>
</table>
5. THERMOCHEMICAL EXPERIMENTS
   Combustion behaviour experiments
   Decomposition of fuels under pyrolytic conditions
   Emissions from combustion
   Domestic pellet stove
   Combustion runs
   Flue gas sampling
   Emissions from torrefaction
   Tubular torrefaction reactor
   Torrefaction runs
   Flue gas sampling
   Analysis of POPs: extraction, clean-up and instrumental analysis

6. THE EFFECT OF UPGRADING ON THE PERFORMANCE OF FUELS
   Reduction of food waste content
   Effect of food waste content on combustion behaviour

7. HOW DOES FUEL UPGRADING AFFECT THE POP EMISSIONS?
   Effect of food waste content on POP emissions
   Effect of the degree of contamination of WW

8. TORREFACTION FOR MITIGATION OF POP EMISSIONS?
   Performance of the fuel blends and properties of chars
   Fate of chemical contaminants
   Assessment of the PCDD and PCDF emissions from torrefaction

9. CONCLUSIONS AND FUTURE WORK
   Future work
   ACKNOWLEDGMENTS
   REFERENCES
ABSTRACT

Incineration with energy recovery is the main disposal strategy for waste that cannot be reused or recycled, and a well-established source of energy in Europe, especially in Sweden where 2.2 Mtonnes of waste including domestic and imported municipal solid waste (MSW) and waste wood (WW) were combusted during 2015. However, owing to its inherent heterogeneous composition, inclusion of such waste in Waste-to-energy (WtE) technologies is challenging. These heterogeneities may lead to operationally-related issues in the WtE facilities and contribute to toxic emissions, which can be reduced by waste pre-treatment technologies.

This thesis examines the variations in the composition of MSW and WW streams used as a fuel supply in WtE facilities after undergoing waste pre-treatment technologies, and the effect of fuel composition on its combustion behaviour and formation of persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The overall objective is to contribute to a more thorough understanding of the selection of waste pre-treatment technologies to mitigate harmful emissions into the atmosphere when waste fuels are combusted in WtE facilities.

This thesis describes the high variability of chemical and material contaminants in domestic and imported WW and suggests adaptation of WW pre-treatment techniques to produce fuels with a low potential for generating pollutants. A comparison of mechanical solid waste pre-treatments revealed that screening and shredding is more efficient than extrusion for reducing emissions of pollutants such as PCDDs and PCDFs in combustion. The evaluation of the combustion behaviour of MSW-based fuels showed a three-stage oxidative decomposition and an acceleration of the decomposition of the MSW compared to the lignocellulosic materials, which may be attributed to the presence of food waste and plastics in the MSW. Combustion tests of fuel blends containing WW and MSW-based fuels with different food waste content suggested that WW, not food waste content, is the key factor for the formation of PCDDs, PCDFs, and polychlorinated biphenyls (PCB), benzenes (PCBzs) and phenols (PCPhs). Torrefaction may be a suitable technology for improving the properties of waste as a fuel e.g. due to its low PCDD and PCDF emissions.
SAMMANFATTNING

Förbränning med energiåtervinning är det huvudsakliga sättet att ta hand om avfall som inte kan återanvändas eller återvinnas. Det är en väletablerad energikälla i Europa och särskilt i Sverige där 2,2 miljoner ton avfall, däribland inhemskt och importerat hushållsavfall och returträ, förbrändes under 2015. På grund av den heterogena sammansättningen hos hushållsavfall och returträ är förbränning av dessa material i anläggningar med energiåtervinning (så kallade WtE-anläggningar) förknippade med en del driftsrelaterade utmaningar. Det kan även ge upphov till miljöfarliga utsläpp, som dock kan reduceras genom förbehandling av avfallet.

I denna avhandling har variationer i sammansättningen hos hushållsavfall och returträ som förbränns i WtE-anläggningar undersöks. Effekten av bränslemixens sammansättning och ev förbehandling på bränslets förbränningsegenskaper samt bildning av långlivade organiska föroreningar (så kallade POPar) såsom polyklorerade dibenso-p-dioxiner och polyklorerade dibensofuriner vid förbränning har utvärderats. Det övergripande målet är att bidra till en djupare förståelse av hur valet av förbehandlingsteknik för avfall kan bidra till att minska skadliga utsläpp till luft när avfallsbränslen förbränns i WtE-anläggningar.

Denna avhandling beskriver den stora variabiliteten av metall- och materialföroreningar i inhemskt och importerat returträ och föreslår förbehandlingstekniker för att producera bränslen med låg potential att generera föroreningar. En jämförelse av mekaniska förbehandlingstekniker visade att mekanisk sönderdelning och separering (krossning och siktning) är mer effektivt än s.k. högtrycks-pressning för att minska utsläppen av föroreningar som dioxiner och furaner vid förbränning. Utvärderingen av bränslemixar innehållande hushållsavfall uppvisade en oxidativ nedbrytning i tre steg vid förbränning, och en accelererad nedbrytning av avfalls materialet jämfört med vedmaterialet i bränslet, troligen som effekt av innehållet av matavfall och plast i hushållsavfallet. Förbränningsförsök med bränsleblandningar av returträ och hushållsavfall med olika innehåll av matavfall visade att mängden returträ, och inte mängden matavfall, är den viktigaste faktorn för bildning av dioxiner, furaner, klorbifenyler, klorbensener, och klorfenoler. Torrefiering kan vara en lämplig teknik för att förbättra avfallets bränsleegenskaper, t.ex. på grund av dess låga emissioner.
### Abbreviations & Definitions

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCA</td>
<td>chromated copper arsenate</td>
</tr>
<tr>
<td>CHP</td>
<td>combined heat and power plant</td>
</tr>
<tr>
<td>DC</td>
<td>demolition and construction wood</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>DTG</td>
<td>derivative thermogravimetric curve</td>
</tr>
<tr>
<td>EFF</td>
<td>extruder fuel fraction</td>
</tr>
<tr>
<td>GC-HRMS</td>
<td>gas chromatography – high resolution mass spectrometry</td>
</tr>
<tr>
<td>FF</td>
<td>fuel fraction</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HCB</td>
<td>hexachlorobenzene</td>
</tr>
<tr>
<td>HHV</td>
<td>higher heating value</td>
</tr>
<tr>
<td>I-TEQ</td>
<td>international toxic equivalents</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>IWM</td>
<td>integrated waste management</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating value</td>
</tr>
<tr>
<td>MBT</td>
<td>mechanical biological treatment</td>
</tr>
<tr>
<td>MHT</td>
<td>mechanical heat treatment</td>
</tr>
<tr>
<td>MSW</td>
<td>municipal solid waste</td>
</tr>
<tr>
<td>MSWr</td>
<td>municipal solid waste rejected</td>
</tr>
<tr>
<td>MVDA</td>
<td>multivariate data analysis</td>
</tr>
<tr>
<td>OPLS-DA</td>
<td>orthogonal partial least squares discriminant analysis</td>
</tr>
<tr>
<td>PAH</td>
<td>polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PCA</td>
<td>principal component analysis</td>
</tr>
<tr>
<td>PCB</td>
<td>polychlorinated biphenyl</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>PCBz</td>
<td>polychlorinated benzene</td>
</tr>
<tr>
<td>PCDD</td>
<td>polychlorinated dibenzo-(p)-dioxin</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>polychlorinated dibenzo-(p)-dioxin and dibenzofuran</td>
</tr>
<tr>
<td>PCDF</td>
<td>polychlorinated dibenzofuran</td>
</tr>
<tr>
<td>PCN</td>
<td>polychlorinated naphthalene</td>
</tr>
<tr>
<td>PCP</td>
<td>pentachlorophenol</td>
</tr>
<tr>
<td>PCPh</td>
<td>polychlorinated phenol</td>
</tr>
<tr>
<td>PIC</td>
<td>product of incomplete combustion</td>
</tr>
<tr>
<td>POPs</td>
<td>persistent organic pollutants</td>
</tr>
<tr>
<td>PUFP</td>
<td>polyurethane foam plug</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
</tr>
<tr>
<td>RDF</td>
<td>refuse-derived fuel</td>
</tr>
<tr>
<td>RW</td>
<td>recovered wood</td>
</tr>
<tr>
<td>SRF</td>
<td>solid recovered fuel</td>
</tr>
<tr>
<td>STA</td>
<td>simultaneous thermal analysis</td>
</tr>
<tr>
<td>(T_{bo})</td>
<td>burnout temperature</td>
</tr>
<tr>
<td>TCDD</td>
<td>tetrachlorodibenzo-(p)-dioxin</td>
</tr>
<tr>
<td>TEF</td>
<td>toxic equivalency factor</td>
</tr>
<tr>
<td>TEQ</td>
<td>toxic equivalents</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>TG-FTIR</td>
<td>thermogravimetric - Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>(T_i)</td>
<td>initial temperature</td>
</tr>
<tr>
<td>US EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>WEE</td>
<td>waste electrical and electronic equipment</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WP</td>
<td>wood pellets</td>
</tr>
<tr>
<td>WtE</td>
<td>waste-to-energy</td>
</tr>
<tr>
<td>WW</td>
<td>waste wood</td>
</tr>
</tbody>
</table>
Definitions

Waste: “Any substance or object which the holder discards or intends to or is required to discard” [1].

Waste Fuel: waste or combustible fraction obtained after applying solid-waste treatment technologies for removing and recovering materials from the waste fraction.

Municipal solid waste (MSW): Non-hazardous waste, mainly household or household-like waste collected by local authorities. It includes commercial waste, institution waste and non-process-related industry waste. It comprises food waste and combustible materials, glass or metal. Waste from municipal services such as waste or water sludge is excluded.

Refuse-derived fuel (RDF): Combustible fraction obtained after removing recyclable and reusable components from the MSW by applying mechanical treatments such as shredding, screening or magnet separation to the MSW.

Solid recovered fuel (SRF): This is a type of RDF, produced in compliance with the European standard EN-15359 [2] to be utilized for energy recovery in incineration plants. SRFs have to meet limit values for three parameters: energy content, mercury content and chlorine content.
LIST OF PUBLICATIONS

This thesis is based on the following papers, which are referred to with Roman numerals.


Published papers are reproduced with permission from the publisher (Elsevier Science)
Author’s contributions

Paper I
The author participated in the planning of the study. She was responsible for the data evaluation and interpretation, and writing the paper.

Paper II
The author was responsible for planning the study and for the fuel preparation, characterization of the material and preliminary experiments. Data evaluation and interpretation was carried out with co-authors at York University. She was responsible for a major part of the writing of the paper.

Paper III
The author was responsible for planning the experiments and fuel preparation. She carried out the experiments in collaboration with her co-authors. She was responsible for sample treatment, data evaluation and interpretation and writing the paper.

Paper IV
The author planned and carried out the experiments as well as carrying out the laboratory work in collaboration with her co-authors. She was responsible for a major part of data evaluation and interpretation and writing the paper.
1. THE IMPORTANCE OF WASTE IN TODAY´S SOCIETY

As the world’s population grows, a broad spectrum of issues related to food, water, medical care and global warming, to mention a few, arise. Waste occupies a prominent position among all these concerns. Waste-related problems were predicted, but were not expected to emerge as fast or with such magnitude [3]. Today, developed nations are facing the challenge of dealing with huge amounts of waste whilst attempting to move towards an ideal zero-waste society. In order to achieve that aim, societies are implementing waste policies, using all the technologies available and educating communities on waste reduction.

Figure 1. The waste hierarchy [1].

The European Waste Framework Directive (2008/98/EC) [1] established the waste hierarchy (Figure 1) which shows the order of preference for reducing or managing waste, from prevention as the most preferred option, to landfill disposal as the least preferred. In between, there is a wide variety of options: re-using, recovering and recycling materials (composting) and energy recovery from waste (e.g. incineration, anaerobic digestion, gasification etc). There is no “one size fits all” solution for waste treatment. Some waste streams fit perfectly into one of these options. For example, paper, glass or metal can easily be recycled, while other waste such as municipal solid waste
(MSW) needs a combination of different waste management approaches because of its complexity. In addition, there will always be a fraction remaining whose further processing would result in higher economic costs and/or environmental impact than benefits [4]. For many years, this remaining waste fraction was placed in landfill. However, due to their negative environmental impact, there has been a steady decrease in the number of landfill sites in Europe [5]. In particular, the disposal of combustible waste in landfills has been banned in Sweden since 2005 [6]. Countries are moving towards alternative ways of treating waste and, currently, incineration is among those approaches for diverting this remaining waste fraction away from landfill disposal.

MSW, also known as mixed residual waste or household waste, ideally consists of the remaining waste fraction after recycling has taken place in households, but it usually contains unsorted waste too. In addition, MSW includes non-hazardous waste generated in commercial establishments and institutions as well as non-process industry waste [3]. It consists mainly of food waste, plastics, paper, cardboard and textiles. The statistical office of the European Commission (Eurostat) estimated that 239 Mtonnes of MSW were generated by the 28 EU Members States during 2014 [5], giving an average of 475 kg of MSW per capita. Sweden contributed approximately 4.4 Mtonnes [7]. During 2015, 2.2 Mtonnes of Swedish MSW was used for energy recovery, 49% of the total tonnage of treated household waste [8]. MSW can be combusted as it is or undergo a pre-treatment stage. This pre-treatment stage changes the physical and chemical properties of the MSW and waste turns into fuel.

Converting waste to fuel

The process of converting waste into fuel is carried out at recovery facilities where the waste is treated using a number of solid-waste processing technologies, hereinafter referred to as mechanical, biological or mechanical heat pre-treatments. The aim of these processes is to recover as many recyclable materials as possible while improving the fuel properties of the waste to increase the yields from energy recovery processes. As a result, the size distribution and the composition of the waste becomes more homogeneous. An increase in the energy density of the waste is also achieved by reducing the moisture content and/or minimizing the ratio of non-combustible materials in the waste, resulting in an increase in the amount of combustible materials (paper, cardboard and plastics) [4]. After this process, the waste has turned into a fuel known as refuse-derived fuel (RDF), ready for combustion. When RDF is produced to meet the specific criteria established by the European standard EN 15359 [2], it is categorized as solid-recovered fuel (SRF).
Waste Incineration

Incineration with energy recovery, also referred to as Waste-to-energy (WtE), is the best known and most widespread technology for recovery of energy from waste. It ideally involves the conversion of the combustible materials contained in the waste into inorganic matter (fly and bottom ash) and flue gas with a subsequent release of heat. In practice, organic residues and products of incomplete combustion (PIC) are also formed. Different waste fractions can be combined and co-combusted. The two main advantages of incineration are the considerable reduction in volume (80 – 90 %) and mass (70 – 80 %) of the original waste [9] (Figure 2), and the potential to produce energy from the waste. Energy is produced by using the hot gases to heat up water and create steam which is fed into a turbine to generate electricity or used for heating [4].

![Diagram](image)

Figure 2. Schematic of the product distribution obtained when MSW is incinerated in a grate system (Source: Waste-to-Energy Masterclass by N. Alderweireldt, J. De Greef and J. Van Caneghem at ISWA 2015 World Congress, Antwerp, September 2015).

Waste incineration is widely accepted in Sweden where, during 2015, a total of 17 TWh of energy were produced from waste. At present, there are 33 incineration plants for household waste [8] which together have a higher incineration capacity than the domestic waste availability. For that reason, a total of 1.3 Mtonnes of wastes for energy recovery, including MSW, waste wood or industrial and commercial waste, were imported by Sweden during 2015 [8] primarily from Norway, Great Britain, and Ireland. In particular, imported waste wood fuel, mainly from packaging and demolition activities, has become a fairly stable fuel source for the Swedish district heating plants [10].
Drawbacks of incineration

Despite the important mass and volume waste reduction and energy recovery achieved, waste incineration has a poor reputation in many countries due to the potential negative impact of its products on the environment and human health. The characteristics of these products are dependent on the waste burnt, operating conditions and incineration technology used [3]. Emissions of acid gases, metals and persistent organic pollutants (POPs) such as dioxins are among the main concerns. Certainly, dioxin (polychlorinated dibenzo-\textit{p}-dioxin and polychlorinated dibenzofuran) emissions have attracted significant attention due to their high toxicity [11, 12].

The relationship between MSW incineration and dioxins in the products was discovered in the 1970s [13]. The high temperatures reached in the combustion zone (1100 – 1200 °C) destroy those dioxins present in the waste during the incineration process. It is during the post-combustion zone i.e. during cooling down (450 – 300 °C) of the flue gases, that the formation of dioxins occurs [14, 15]. Great improvements in incineration technologies and operating conditions over the last 30 years have efficiently reduced emissions and ensured that the gases emitted meet the limits established by the legislation. For example, since 1985, the total emissions of dioxins from all the Swedish waste incineration plants have reduced from 100 g to less than 1 g per year with the heavy metal emissions having been reduced by almost 99% [16].

Although the most effective strategy for reducing and limiting the formation of dioxins is by means of technical improvements and prevention of conditions favourable for formation (i.e. controlling the CO levels during the process [17, 18], and the combustion and post-combustion zone temperatures), we should not forget that the composition of the fuel is also a key component in dioxin formation. The formation of dioxins and other chlorinated POPs which have a negative impact on the environment and human health would not occur if chlorine was not available in the fuel. In addition, the presence of metals, such as copper or iron, in the particulate matter is also known to facilitate the formation of dioxins [19-22]. In other words, reducing the concentrations of chlorine, copper, iron or any other type of elements that may favour the formation of dioxins in the fuel is a step closer to limiting such formation. Therefore, it is crucial to assess the composition of the waste streams which are destined to be turned into fuels with the aim of selecting the most suitable waste pre-treatment technologies for the waste-to-fuel conversion process and ensure the production of fuels with high quality and low environmental impact.
Aims of this thesis

MSW and waste wood (WW) are waste fuels used in the WtE process, which is a well-established source of energy in many European countries; of these countries, Sweden leads the way [16]. Although Sweden carries out WtE in a very efficient way with airborne emissions having drastically declined over the years, it is necessary to keep improving further all the steps involved in this process, from the production of waste fuels to the incineration technologies used, to guarantee a minimum impact on the environment and wildlife.

This thesis focuses on three fuels for WtE processing: MSW, RDF and WW. The overall aim is to investigate how the performance in the co-combustion process of these fuels was affected by the changes in their composition due to the use of different solid-waste pre-treatments. The knowledge gained of the selection of the most suitable solid-waste pre-treatment techniques will contribute to the production of quality fuels. These fuels, when combusted in WtE facilities, will generate lower dioxin emissions, which could mitigate the environmental impact of the combustion process.

The specific issues addressed in this thesis include:

- Assessment of the chemical and material contamination of WW fuel over time (Paper I).
- Analysis of the combustion behaviour of MSW and RDF obtained using different mechanical solid-waste pre-treatments technologies (shredding and screening and extrusion) (Paper II).
- Evaluation of the WW, MSW and RDF performance in terms of POP emissions in actual co-combustion (Paper III).
- Evaluation of the use of torrefaction as a pre-treatment technology in WW, MSW and RDF and its impact on dioxin formation (Paper IV).

Connections between the different studies are shown in Figure 3.
Figure 3. Brief description of the aim of each paper included in this thesis and their connections. Waste wood composition is the cornerstone of Paper I and its conclusions support the results obtained in Papers II – IV. Paper III is a follow-up study of Paper II, and Paper IV is a follow-up study of Paper III. Both Papers II and IV evaluate the effectiveness of solid-waste pre-treatments.
2. CONTAMINANTS & POLLUTANTS

Acquiring knowledge of the contaminants in waste is essential for selecting the most suitable solid-waste pre-treatment technologies. In addition, contaminants may be the key to understanding the performance of a fuel and the formation of some pollutants during thermal processes.

**Contaminants**

Contaminants are unwanted substances that are present in a material. This thesis includes a detailed study of chemical and material contaminants in waste wood (Paper I).

*Waste wood chemical contaminants* are trace elements derived from agents that were used to treat the timber in order to extend its service life or prevent physical damage and pest infection, but can also be pigments used in paints [23]. These elements occur in biomass as well, but their concentration is several orders of magnitude larger than in natural wood. They principally cannot be mechanically separated from the main source. In Paper I, 22 trace elements seen as chemical contaminants were analyzed in waste wood samples. The trace elements included were: S, Cl, Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn. Some of these elements such as Cl, Fe and Cu were also studied in MSW and RDF due to their relevance in the formation of chlorinated organic pollutants during combustion (Paper III) and torrefaction (Paper IV). In particular, Cl was used as an indicator of the efficiency of different solid-waste pre-treatments to reduce the food waste content in MSW and RDF (Paper II). The presence of the wood preservative pentachlorophenol (PCP) in waste wood was examined for Paper III.

*Waste wood material contaminants* are unwanted material fractions that principally can be separated from the waste wood i.e. by sorting or by using mechanical pre-treatments such as sieving, magnetic fields or eddy current separation [23]. A total of 17 different waste wood material contaminants were identified in Paper I. The issue of polyvinyl chloride (PVC) as a material contaminant in MSW was discussed in Paper II.
Pollutants

“Pollutants are substances in amounts that are detrimental to humans, animals, plants or properties” [3].

This thesis mainly focuses on two classes of persistent organic pollutants (POPs) which are related to MSW incineration [13]: polychlorinated dibenzo-\(p\)-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) which are often referred as ‘dioxins’. These pollutants are formed as a result of thermal processes and some of them are highly toxic. In addition to PCDDs and PCDFs, polychlorinated biphenyls (PCBs), polychlorinated benzenes (PCBzs), polychlorinated phenols (PCPhs) and polycyclic aromatic hydrocarbons (PAHs) were also investigated in one of the studies (Paper III). Most of these compounds have a negative impact on the environment and human and wildlife health. All of them are, in some way, related to the incineration process [13, 24], hence their importance in this thesis.

**PCDDs and PCDFs**

These chlorinated aromatic hydrocarbons compounds have a very similar molecular structure (Figure 4). The dibenzo-\(p\)-dioxin molecule consists of two benzene rings linked by two oxygen bridges, while in the dibenzofuran molecule, the two benzene rings are linked by one oxygen bridge and one carbon-carbon bond. Chlorine atoms can attach to carbon atoms in eight different positions labelled 1 – 4 and 6 – 9 (Figure 4). As a result, there are 75 different PCDD and 135 different PCDF congeners.

*Figure 4. General molecular structure of PCDD (left) and PCDF (right).*

PCDDs and PCDFs also have similar properties. They are very stable, especially PCDFs, lipophilic compounds resulting in a great tendency to accumulate in the fatty tissue of living organisms, including humans. Such compounds are also prone to significant biomagnification and persistence in the environment [11]. Dioxins can be formed through natural processes such as forest fires or volcanic eruptions [25]. However, human activity has been the main source of dioxin formation over the past two centuries [12]. Because of their persistence in the environment, they were included in the Stockholm
Convention on POPs [24]. Dioxins are formed as unwanted by-products from thermal processes [25, 26], industries such as pulp and paper [27] or metal smelting plants [28, 29]. In 1977, dioxins were identified in MSW incineration effluents (ash and flue gas) for the first time [13]. Since then, most of the processes related to the formation of dioxins have been regulated [12] with recent inventories of sources of dioxins identifying open fires in agriculture and forests and the burning of waste in the open air as major sources of PCDDs and PCDFs [30]. They have no industrial use, so are not commercially produced except for small amounts for research purposes. As they are so important in MSW incineration processes, information about PCDDs and PCDFs was given in Papers III and IV.

In combustion processes, the formation of PCDDs and PCDFs is dependent mainly on the combustion efficiency, which in turn depends on the temperature in the combustion and post-combustion zones, oxygen supply, residence time of the gases and turbulence in the combustion zone [31]. PCDD and PCDF formation also depends on the composition of the fuel. The presence of chlorine in the fuel is essential for the formation of chlorinated organic pollutants: potential sources of chlorine are Cl₂, Cl radicals or chlorinated precursors, including chlorinated benzenes and phenols [32]. Copper, in particular the copper chloride species CuCl and CuCl₂, is a very efficient catalyst in the formation of PCDDs and PCDFs [21, 22, 33, 34], as well as other metals and metal oxides such as iron [21] or chromium [35], to mention a few (all of them with lower catalytic efficiency than copper). In contrast, sulphur compounds (elemental sulphur or sulphur dioxide [36, 37] are known to be inhibitors of PCDD and PCDF formation.

**Related compounds**

Many compounds are formed during waste combustion in addition to the already mentioned PCDDs and PCDFs. Among others, there is a group of chlorinated compounds that are of interest because of their similarity to dioxins in terms of chemical and physical properties and toxic effects. They are referred to as ‘dioxin-like’ compounds and include compound groups such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs), the latter not being included in this work.

Polychlorinated biphenyls (PCBs) are a large group of chemicals composed of two benzene rings linked by a carbon-carbon bond with up to 10 hydrogen atoms capable of being substituted with chlorine atoms (Figure 5), resulting in 209 congeners. A total of 12 PCB congeners, those with a coplanar structure, exhibit ‘dioxin-like’ properties [12, 38]. They have a significantly high heat capacity and low conductance and so, for that reason, were extensively used as one of the main components of insulating fluids in
CONTAMINANTS & POLLUTANTS

electrical equipment in power plants from the beginning of the last century until the 1970s when their use was restricted because of health and environmental concerns [39]. PCBs were one of the original twelve POPs included by the Stockholm Convention [24]. Parties to the Stockholm Convention can no longer produce PCBs, but existing equipment containing PCBs can be used until 2025 [24]. PCBs may be formed during combustion of waste [24] and that is why they were investigated for Paper III.

Figure 5. General molecular structure of PCB.

Polychlorinated benzenes (PCBzs) form a group of 12 congeners whose molecular structure consists of a benzene ring with 1 to 6 chlorine substituents (Figure 6). The fully chlorinated species, hexachlorobenzene (HCB), is one of the target compounds in the Stockholm Convention [24]. It mainly originates from industrial activities [40] and combustion processes [41, 42]. It was used as fungicide in many countries until the 1970s. In 2006, it became clear that some pigments were contaminated with HCB [43]. It is toxic for human beings and rats, causing adverse effects in their reproductive and immune systems [44]. PCBzs were investigated for Paper III.

Figure 6. General molecular structure of PCBz (left) and PCPh (right).

Polychlorinated phenols (PCPhs) consist of a benzene ring with a hydroxyl group attached with 1 to 5 chlorine substituents (Figure 6), resulting in 19 congeners. The most important PCPh is the biocide and pesticide pentachlorophenol (PCP). It has been extensively used since the 1930s as a timber preservative and is nowadays mainly used on utility poles and cross-arms [45]. The use of PCP has already been banned or restricted by many nations, including the EU Members [45]. PCP (and its salts and esters) became
one of the POPs targeted by the Stockholm Convention in 2015, due to its high toxicity [24]. PCP content in waste wood was described for Paper III.

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds composed of multiple aromatic rings (Figure 7). The US EPA (United States Environmental Protection Agency) has listed 16 priority PAHs [46] because of their toxicological and environmental concern; they are referred as the 16 EPA PAHs. PAHs are products of incomplete combustion and are formed during waste incineration [47]; PAHs were investigated for Paper III.

![Molecular structure of the 16 EPA PAHs.](image)

**Toxicity**

As previously mentioned, PCDDs, PCDFs and PCBs are very stable compounds and prone to biomagnification. Their toxicity is related to their ability to bind and activate the aryl hydrocarbon receptor (AhR). AhR is a receptor protein present in the tissues of many organisms which is activated by planar polyhalogenated aromatic hydrocarbons such as PCDDs, PCDFs and ‘dioxin-like’ PCBs, among others [11]. Not all the 75 PCDD and 135 PCDF congeners are toxic. Only those with chlorine in the 2, 3, 7, 8 positions (Figure 4) exhibit toxic properties, which considerably reduces the number of toxic congeners to 7 PCDDs and 10 PCDFs. In the case of PCBs, only those
congeners with no more than one chlorine substituent in the ortho-position (2, 2’, 6, and 6’) and a minimum of four in lateral positions (3, 3’, 4, 4’, 5, 5’) produce the planar configuration that allows them to bind to the AhR [48]. The PCBs without ortho-substituted chlorine atoms are usually referred as non-ortho or co-planar PCBs. In addition, they may have chlorine substituents in the para (4 and 4’) and meta positions, (3, 3’, 5 and 5’), resulting in 12 PCB toxic congeners (Figure 5).

The main acute effect of PCDDs and PCDFs on humans is chloracne. An increase in the risk of cancer, especially reproductive-related ones, and effects on the endocrine system have also been reported [49]. Toxicity assessment of dioxins and ‘dioxin-like’ PCBs uses the Toxic Equivalent Factors (TEF) measure which expresses the toxicity of dioxins, furans and ‘dioxin-like’ PCBs in comparison to the most toxic dioxin, 2,3,7,8-TeCDD. In other words, the TEF value of 2,3,7,8-TeCDD has been set to 1, the maximum, with the other toxic PCDDs, PCDFs and ‘dioxin-like’ PCBs being assigned TEF values relative to these most toxic congeners (Table 1). However, living organisms are not usually exposed to a single toxic compound, but to a “cocktail” of them, and this also applies to dioxins and ‘dioxin-like’ compounds. The combined exposure, total toxic equivalent (TEQ), can be calculated as the sum of the products of the concentration of each compound in that sample multiplied by its TEF. These factors were last revised in 2005 by the World Health Organization (WHO) [50].
**Table 1.** WHO 2005 Toxic equivalent factors (TEFs) of PCDDs, PCDFs and PCBs [38].

<table>
<thead>
<tr>
<th>Compound</th>
<th>TEF</th>
<th>Compound</th>
<th>TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-TeCDD</td>
<td>1</td>
<td>3,3',4,4'-TeCB (#77)</td>
<td>0.0001</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>1</td>
<td>3,4,4',5-TeCB (#81)</td>
<td>0.0003</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDD</td>
<td>0.01</td>
<td>3,3',4,5-PeCB (#126)</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDD</td>
<td>0.1</td>
<td>3,3',4,4',5'-HxCB (#169)</td>
<td>0.03</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDD</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCDD</td>
<td>0.0003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCDF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-TeCDF</td>
<td>0.1</td>
<td>2,3,3',4,4'-PeCB (#105)</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDF</td>
<td>0.03</td>
<td>2,3,4,4',5-PeCB (#114)</td>
<td>0.00003</td>
</tr>
<tr>
<td>2,3,4,7,8-PeCDF</td>
<td>0.3</td>
<td>2,3,4,4',5-PeCB (#118)</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDF</td>
<td>0.1</td>
<td>2,3,3',4,4',5'-PeCB (#123)</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDF</td>
<td>0.1</td>
<td>2,3,3',4,4',5'-HxCB (#156)</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.1</td>
<td>2,3,3',4,4',5-HxCB (#157)</td>
<td>0.00003</td>
</tr>
<tr>
<td>2,3,4,6,7,8-HxCDF</td>
<td>0.1</td>
<td>2,3,3',4,4',5-HxCB (#167)</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.01</td>
<td>2,3,3',4,4',5,5'-HxCB (#189)</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,4,7,8,9-HpCDF</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCDF</td>
<td>0.0003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# numbering according to the IUPAC
3. THE IMPORTANCE OF WASTE COMPOSITION

The most crucial factors in determining the feasibility of a waste as fuel is the origin of the waste and its energy content [51]. The nature of the waste has a strong influence on its composition and, as a result, in its quality as fuel. Waste has a complex composition which is complicated further when mixed with other combustible waste fractions for co-combustion. Waste composition also has a great impact on the combustion performance of the fuels (Paper II), formation of toxic organic pollutants in thermal processes (Papers III – IV) and creation of technical problems in the boilers. In order to operate an incineration plant continuously, it needs a fairly stable supply of waste and a reasonable estimate of the waste composition over the year. However, estimating the amount and composition of waste such as MSW or waste wood requires an in-depth knowledge of the waste collection areas, making it difficult to forecast. Hence, it is important to carry out case studies on waste composition (Paper I) which at least provide some indications about current composition trends of a specific fuel.

Variation in MSW composition

MSW includes non-hazardous waste generated by households, commercial establishments, institutions and non-process-related industrial waste such as paper and paperboard [3]. Mechanical pre-treatments turn MSWs into homogenous fuels (RDF and SRF) to be used in WtE processes, provided they meet certain requirements especially regarding energy content of the fuel. The lower heating value (LHV) of waste used as fuel, closely related to the waste’s composition, must be at least 6 MJ kg⁻¹ throughout the year (seasons) [51].

The composition of MSW reflects the social-economic situation and climate conditions of the collecting area but also the cultural behaviour of that community, laws governing waste management and technical factors such as availability of recycling systems in the municipalities [51-53]. As an example, climatic conditions such as snow and precipitation have a strong influence on
the moisture content of the waste, together with food waste [51], and combustibility of the fuel which may be subject to seasonal variations. For these reasons, any data regarding average composition of MSW in a large area must be viewed cautiously. The average composition of unsorted household waste generated by one-family households in Sweden during 2015 is shown in Figure 8 as example [7].

![Figure 8. Average composition of MSW from a Swedish household in 2015 [7]](image)

**Importance of food waste in MSW**

Food waste is putrescible solid material, animal or vegetal, resulting from food handling processes such as cooking, serving, sale or storage [3]. On average, food waste accounts for 24% (Figure 8) of the MSW in Sweden in municipalities with separate food waste collection, and up to 40% [7] in those without this collection system. Implementation of a separate collection of food waste and introduction of guidance by governmental institutions about how to reduce this waste [54] has slightly reduced the proportion of food waste in MSW over the last few years. Reduction of food waste is a way of avoiding wasting resources and producing unnecessary emissions, while separately collected food waste can be used as feedstock in the production of renewable energy such as biogas, compost or fertilizers [4]. In 2015, the amount of food waste being biologically treated in Sweden increased by 10% from 2014 [8].
The presence of food waste in MSW to be used as fuel has some drawbacks. The moisture content of the fuel increases, resulting in a lower energy content [51]. Together with plastics, food waste has been identified as the main component responsible for the chlorine content of MSW [55, 56], resulting in an increase in the potential formation of toxic chlorinated pollutants such as dioxins and furans [57, 58] under specific conditions. The impact of the food waste content on the combustion behaviour and combustion and torrefaction emissions was studied in detail for this thesis (Papers II – IV).

**Variation in waste wood (WW) composition**

Waste wood is wood that has been used previously for various purposes, ending up in the waste stream. It comprises packaging, pieces of furniture or wood from construction activities and small amounts of any type of construction material such as stone, ceramic materials, brick or concrete. Forestry residues and industrial by-products are not considered to be WW [59].

The timber used in the production of wood items is, of course, the main component of WW and it also has a great influence on the final composition of the waste. However, paints, preservatives and coating applied to timber to extend its service life or prevent physical damage [23, 60-64], together with substances which have been in contact with the wood over its life [23, 64], are considered as the main components responsible for the complexity of WW composition and the degree of contamination [23, 64, 65]. In addition, Sweden has considerably increased the import of WW to be used as fuel [8, 66] over recent years. The use of imported WW from countries with less strict laws governing the use of wood preservatives has added a certain degree of complexity to the composition of this fuel, and made predicting the composition of WW to be combusted in Swedish plants more difficult.

**Paper I** describes a case study investigating how the chemical and material contaminants in WW have changed over nine years. For this study, 500 WW samples, including domestic and imported WW (Figure 9), were collected between September 2004 and March 2013 from a co-combustion plant owned by Vattenfall and situated in Nyköping (Sweden). It is important to note that, from 2011, all the WW started to be screened at the collection plants in order to remove fines. Fines are small particles (< 4 mm) which contain high quantities of paint flakes and small pieces of plastics or metals [23, 64]. A total of 47 chemical and physical parameters were measured from the samples, including energy and ash content, trace element content, particle size distribution and material contaminants (Figure 10). A detailed description of
The importance of waste composition can be found in Paper I. 

**Figure 9.** Proportion (wt.%) of imported waste wood (WW) fuel burnt at Vattenfall co-combustion facility from 2006 to 2012 (Paper I).

**Figure 10.** Parameters measured in the waste wood (WW) fuel samples collected at Vattenfall co-combustion facility over a specific sampling period (Paper I).

The analysis of the WW samples collected showed that, on average, their calorific value was about 13.5 MJ kg$_{ar}^{-1}$ (ar: as received), which is slightly higher than the calorific values for biomass such as pine chips (12.5 MJ kg$_{ar}^{-1}$) or MSW (6 – 10 MJ kg$_{ar}^{-1}$) [51, 67]. Moisture content was 23% on average. However, this figure should be treated with caution since moisture content is also dependent on the climate and storage conditions.
The variation in the material contaminant content was studied in 329 WW samples (Figure 10). The identified material contaminants were divided into 17 different categories. On average, material contaminants accounted for 1.1 % of the WW weight, with stone (19 – 44 %), plastic (14 – 25 %) and iron (14 – 22 %) being the three materials accounting for the highest mass ratio in the studied samples (Figure 11). Most of the material contaminants identified were related to demolition and construction activities.

Figure 11. Variation in the proportion of material contaminants (wt.%) in waste wood (WW) fuels from 2008 to 2013 (Paper I).

To determine the variation in the chemical composition, the concentrations of a total of 22 trace elements were measured in all 500 WW samples (Figure 10). Particular attention was paid to the concentrations of volatile metals and
chlorine due to their importance in the formation of toxic chloroorganic compounds in waste combustion [21, 22, 68, 69]. The evaluation of the maximum, minimum and average concentration for each trace element in each year of study (Figure 12) clearly showed the high variability of the chemical contaminant concentrations in WW over time, which is in agreement with previous studies of WW composition [60, 61].

Some trace elements exhibited particularly high variations: Cr (1.5 – 313 mg kg\(^{-1}\)\(_{ds}\)), Cu (3.6 – 3,200 mg kg\(^{-1}\)\(_{ds}\)), As (0.10 – 270 mg kg\(^{-1}\)\(_{ds}\)) (ds: dry sample). These three elements are associated with chromated copper arsenate (CCA) wood preservative formulations which were widely used from the mid-1930s and banned in Sweden in 1992. As and Cr showed a decreasing trend for their average concentration in WW until 2011, while Cu average concentration fluctuated over the years (Figure 12). Due to the ban on CCA formulations coming into force in 1992, and considering an estimate lifespan of CCA-treated wood to be around 20 – 25 years, one might not expect extensive changes in the CCA concentration until 2012. However, the ban might have changed the fate of the CCA-treated wood from being reused or recycled to be combusted, which could explain the increase in CCA concentration from 2011. Another important factor to consider is the increase of imported WW used over the years, as shown in Figure 9. In the first few years, only 29% of the plant’s fuel was imported, but, by 2012, this had risen to 85%. However, the absence of more precise data about the specific national origin and the quantity of WW fuel imported makes it difficult to establish whether there is a link between the increase in CCA concentration in WW and an increase in the use of imported WW in Swedish co-combustion facilities. Two other trace elements worth mentioning are Cl and Pb, whose levels in the WW fuels decreased by 45% and 30% respectively between 2010 and 2012, coinciding with the implementation of WW screening at the collecting plants by the suppliers.
Figure 12. Variation in the concentrations of chemical contaminants in waste wood (WW) fuels collected at Vattenfall co-combustion plant between 2004 and 2013 (Paper I). The minimum, maximum and average concentrations of each trace element are shown in mg kg\textsubscript{ds}\textsuperscript{-1}, except for Cl and S which are shown in wt\textsubscript{ds}\% (ds: dry sample).
In addition, a comparison between concentrations of the chemical contaminants in the WW fuel in the earlier (2008 – 2009) and later (2012 – 2013) sampling years was carried out by using multivariate data analysis (MVDA) techniques, in particular orthogonal partial least squares discriminant analysis (OPLS-DA). This technique allows the determination of which chemical contaminants had the greatest effect on the variation in the WW composition.

OPLS-DA is a discrimination method that uses a binary matrix $Y$ (here, WW classification based on chemical composition) to decompose the $X$ data (here, concentrations of chemical contaminants in WW) into two types of information – predictive (between-class variation) and orthogonal (within-class variation). The relationship between observations (WW samples) and variables (concentration of chemical contaminants in WW) were visualized using score and loading plots. The score plot reveals the distribution of the observations, while the loading plot shows the distribution of variables. The OPLS-DA analysis was carried out using the SIMCA P+13 software package (Umetrics AB, Sweden).

A total of 23 variables (chemical contaminant concentration in WW) were considered during the 2008 – 2009 and 2012 – 2013 sampling years, yielding a model that generated one predictive and one orthogonal component with good predictive ability ($Q^2Y=43\%$) and total variance ($R^2X=52\%$). The predictive component ($t[1]$) grouped the samples into two clusters as shown in the score plot (Figure 13 (a)), one containing the samples from 2008 – 2009 and the second one containing the samples from 2012 – 2013. It can be seen that clusters were not clearly separated though. Comparison of score and loading plots (Figure 13 (a) and (b)) showed that, for the earlier years, the WW samples contained more Zn, Cd, Cu, Co, As and Hg which are trace elements usually found in the fine fraction [23, 64]. Conversely, WW samples from the latter years were richer in mineral matter (Si, Ca or P). The proximity of Cl and Pb in the loading plot indicates their close relationship to each other, while their separation from the other variables points to two different sources of contaminants within this cluster.

In summary, Paper I found that demolition and construction activities were presumably the main supply of material contaminants in the fuel source. The composition concentration of each chemical contaminant varied widely, confirming great variability in the composition of WW fuels. Results suggest that the current globalization of WW supply points to a need to assess the chemical composition of the WW fuels and apply different pre-treatment techniques to ensure the quality of the fuels and minimize their environmental impact.
Figure 13. OPLS-DA score (a) and loading (b) plots derived from the analysis of the waste wood (WW) samples collected at Vattenfall co-combustion plant during 2008 – 2009 and 2012 – 2013 (Paper I). Each circle and square in the score plot represents a WW sample from the early sampling years; each star and triangle represents a sample from the latter sampling years. Every individual square in the loading plot represents an element that was found in the WW.
4. UPGRADING WASTE TO FUEL

The complex composition and heterogeneity of waste means it has to be upgraded before being used as fuel for WtE. This section describes the waste sources targeted in this thesis and the technologies used for upgrading waste to fuel. A detailed description of the materials used (Table 2), the sampling procedure and the fuel preparation for the production of fuel blends by combining different household waste-based materials and waste wood are presented in this chapter.

Table 2. Summary of the materials used in this thesis, a short description and the papers in which they were studied.

<table>
<thead>
<tr>
<th>FUEL</th>
<th>DESCRIPTION</th>
<th>PAPER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woody materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST / WP</td>
<td>Stemwood / Wood pellets (Virgin biomass)</td>
<td>II-IV</td>
</tr>
<tr>
<td>RW</td>
<td>Recovered Wood (Industrial and demolition and construction wood)</td>
<td>II</td>
</tr>
<tr>
<td>DC</td>
<td>Demolition and construction Wood</td>
<td>III, IV</td>
</tr>
<tr>
<td>Waste wood(WW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSW(r)</td>
<td>Municipal solid waste (rejected) (5 –20 wt.% food waste)</td>
<td>II-IV</td>
</tr>
<tr>
<td>RDF/FF</td>
<td>Refuse-derived fuel / Fuel Fraction (&lt;5 wt.% food waste)</td>
<td>II-IV</td>
</tr>
<tr>
<td>EFF</td>
<td>Extruder fuel fraction (&lt;2 wt.% food waste)</td>
<td>II</td>
</tr>
<tr>
<td>Fuel Blends*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80:20</td>
<td>MSW(r), RDF/FF or EFF combined with WP or RW</td>
<td>II</td>
</tr>
<tr>
<td>60:40</td>
<td>MSW(r), RDF/FF or EFF combined with WP or RW</td>
<td>II</td>
</tr>
<tr>
<td>20:80</td>
<td>MSW(r), RDF/FF combined with ST/WP DC</td>
<td>III, IV</td>
</tr>
</tbody>
</table>

*Blend ratios waste:wood weight (wt.%)
Waste Sources

Waste Wood

Waste wood (WW) chips collected at a recycling centre and waste treatment plant situated in the south of Sweden were used in the studies described in Paper II and are referred to as recovered wood (RW). The WW used in the studies described in Papers III – IV was collected at a combined heat and power plant (CHP) located in the north of Sweden and is referred to as DC. Wood from demolition and construction (DC) and industrial activities is an interesting WW because of its high levels of contaminants and potential to form POPs when used in thermal processes [69, 70]. It was composed mainly of big pieces of woody materials such as furniture, doors or fibre board together with remnants from construction activities such as plastics, cables and isolation materials [70]. Hereinafter, WW will be used as a generic term, while DC will be used in this thesis to refer to the WW (RW and DC) described in Papers III – IV so as to highlight its origin.

Figure 14a. Virgin wood and waste wood used for the combustion and torrefaction studies described in this thesis. From left to right: ST: commercial stemwood pellets (Papers II – IV); RW: recovered wood (Paper II) and DC: demolition and construction wood (Papers III – IV).

Their low ash, metal and POP content [71] meant that commercial stemwood pellets, made of a mixture of bark-free Norwegian spruce and Scots pines, were selected as a reference wood material for comparison with DC. They are referred as wood pellets (WP) in Paper II and as stemwood (ST) in Papers III – IV and in this thesis. A comparison of ST with DC can produce information on how the presence of contaminants in the wood component of the fuel mix affects the physical and chemical properties, the thermal behaviour and emissions.
Household waste

The household waste selected for the studies was the fraction remaining after food waste was manually separated from MSW on an individual basis in households. It is referred to as MSW rejected (MSWr) in Paper II and MSW in Papers III – IV and hereinafter in this thesis. It comprises mainly plastics, paper, cardboard, textiles and 5 – 20 wt.% food waste depending on the efficiency of the separation carried out by the household. This household waste fraction underwent a variety of mechanical treatments with the aim of reducing the particle size, food waste and moisture content of the waste as well as removing the recyclable materials. The household waste fraction can be turned into a homogeneous fuel as described later in this chapter. MSW was collected at a recycling centre and waste treatment plant situated in the south of Sweden.

Some relevant information about the household waste described above is presented in Table 3. Detailed information about chemical composition and energy content of these waste sources is given in Papers II – IV.

Table 3. Selected information about the different waste sources and fuels (Papers II – IV).

<table>
<thead>
<tr>
<th></th>
<th>ST/WP</th>
<th>RW</th>
<th>DC</th>
<th>MSW(r)</th>
<th>RDF/FF</th>
<th>EFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash %ds</td>
<td>2.4</td>
<td>2.0</td>
<td>3.7</td>
<td>24</td>
<td>17</td>
<td>23</td>
</tr>
<tr>
<td>LHV MJ kg ds⁻¹</td>
<td>18.0</td>
<td>17.9</td>
<td>18.9</td>
<td>17.6</td>
<td>22.9</td>
<td>19.3</td>
</tr>
<tr>
<td>Cl %ds</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.27</td>
<td>0.89</td>
<td>0.32</td>
<td>0.50</td>
</tr>
</tbody>
</table>

¹ds: dry sample; ST/WP: steamwood; RW: recovered wood (Paper II); DC: demolition and construction wood (Papers III – IV); MSW(r): municipal solid waste (rejected) RDF and refuse-derived fuel (Papers II – IV); EFF: extruder fuel fraction (Paper II).

Figure 14b. Household waste used for the combustion and torrefaction studies in this thesis. From left to right: MSW: municipal solid waste (Paper II); RDF: refuse-derived fuel (Papers II – IV) and EFF: extruder fuel fraction (Paper II – IV).
From waste to fuel

Using pre-treatment technologies, it is possible to turn household waste into fuel. Pre-treatment technologies are part of what is known as an Integrated Waste Management (IWM) system, a collection of suitable technologies, techniques and management programmes applied to waste in order to reach specific waste management goals [3]. Pre-treatment technologies are selected depending on the potential uses of the waste components: recycling, biological treatment, energy recovery by means of RDF or putting into landfill. There must be a good match between waste/fuel and technology to guarantee the lowest environmental and economic impact [4]. Such technologies can be classified into three groups [4]:

- **Mechanical treatments** attempt to sort out different fractions from the MSW and remove and recover valuable materials, reduce the moisture content and/or the particle size of the waste stream, resulting in a homogeneous fuel. Magnetic separation, eddy current separation, screening, shredding, extrusion or air classification are among the most widely-used mechanical treatments.

- **Mechanical biological treatments** (MBTs) combine mechanical processing and biological treatments such as composting or anaerobic digestion with the objective of transforming the biodegradable fraction in the MSW into a stabilized output [72].

- **Mechanical Heat Treatments** (MHTs) combine mechanical and thermal technologies such as autoclaving to separate different fractions from the MSW to facilitate further processing while sanitizing the waste by reducing the moisture content and destroying bacteria present [73]. Torrefaction used as a thermal pre-treatment for improving the properties of materials as fuels is also considered to be a MHT.

This section describes the mechanical and mechanical heat treatments applied to the waste streams studied for this thesis, used with the aim of improving the quality of the fuel obtained.
Mechanical treatments

Screening

Screening is used to produce an output material with a more homogeneous particle size distribution than the input material, by using surfaces or screens. Drum screens are the most widely-used sieving device; others include disc and vibrating screens [74]. Screening is also extensively used to improve the quality of fuels, such as WW, by separating fines (<4mm) from the input material. Fines contain elevated amounts of chemical contaminants such as chromium, lead, zinc, chlorine or potassium from paint flakes, coating or wood preservatives [59], together with small pieces of plastics, metals and similar materials.

The efficiency of screening as a waste pre-treatment technology for removing chemical contaminants from the WW stream was evaluated for Paper I. In 2010, the levels of chemical contaminants, such as Cl, Pb, Cu and Co, increased considerably in the WW fuel (Figure 15) used at the co-combustion facility owned by Vattenfall in Nyköping. Vattenfall took action and, from 2011, started to ask their international suppliers to screen the WW at the collection plants before delivery to the co-combustion facility in order to remove fines (4 mm) and, thus, reduce the chemical contaminants from the fuel. Data showed that the concentrations of Cl and Pb in WW decreased by 45% and 30% respectively (Figure 15) after implementation of sieving at the collecting plants. However, the levels of these elements remained high and never fell back to the comparatively low levels seen before 2010. A theory explaining the increase of certain chemical contaminants, such as Cl and Pb, in the WW fuel is that there was an increase in the amount of imported wood together with the introduction of supplies from other countries not used before. Unfortunately, it is not possible to draw any firmer conclusion with the information that was available when this study was undertaken. However, detailed information about the country of origin of the WW would definitely help to clarify this issue.

In summary, the findings in Paper I demonstrate that sieving alone is not an effective treatment for reducing the levels of chemical contaminants in WW fuel. The sieved WW fuel still retains pollutants at a level that may give rise to undesirable emissions when it is combusted. The results suggest that adoption of stricter processing requirements is required to obtain a WW fuel with at least the same quality as was achieved when most of the fuel was from within Scandinavia.
Shredding and screening are two mechanical treatments that are usually combined to achieve an effective preparation of RDF from MSW. Shredding reduces the average particle size of the MSW by, for instance, tearing through rubbish bags thus helping subsequent pre-treatments, homogenises the fuel composition and increases its bulk density [75]. Screening is used after shredding to homogenise the particle size of the material. The outputs from shredding and screening MSW are a fine and a coarse fraction (Figure 16). The fine fraction comprises mainly incombustible materials and food waste [57]. The coarse fraction, also known as the fuel fraction (FF), comprises mainly plastic, paper and cardboard and has a lower moisture content than the MSW. FF is considered to be RDF. Shredding and screening are the most widely-used treatments for separating food waste from MSW at waste treatment facilities at present.
The MSW stream was shredded and screened in a grinder (Doppstadt DW 3060) and a 100mm drum screen (Doppstadt SM 518) as a means of reducing the food waste content from 5 – 20 wt.% in the MSW stream to less than 5 wt.% in the fuel fraction. The so-called fuel fraction (FF) was used for **Paper II** to study the influence of food waste content on the fuel’s properties and combustion behaviour. In **Papers III – IV**, FF was referred to as RDF and used for studying the effect of food waste content on combustion emissions and torrefaction products.

**Extrusion in a high pressure press**

Extrusion of MSW in a high pressure press is an emerging mechanical treatment which separates the MSW into a wet and a dry fraction (**Figures 16 and 17**). The mixed waste is held in a chamber and compressed at a high pressure, up to 1000 bar [76], against a perforated extrusion matrix which acts as a screen. The high pressure breaks down the structure of the food waste in the MSW and turns it into a liquid that leaves the chamber through the matrix (**wet fraction**). This fraction undergoes further cleaning if needed, before being used as substrate in anaerobic digestion to produce biogas or being composted. A **dry fraction**, composed mainly of compressed plastic, paper, inert and retained food waste, remains in the press chamber. The **dry fraction** can undergo additional separation processes to remove recyclable materials such as metals, and can be shredded to reduce its size, finally becoming RDF, with a higher calorific value than the original material. In addition, the volume is reduced 5 to 6 times [77] with respect to the mixed waste, facilitating its transport and storage. The **dry fraction** is, on average, 30 – 40 wt.% of the
input depending on the input composition and the effectiveness of the separation process, which may reach 90 – 98 % [77, 78]. Generally, extrusion is a more effective method than shredding and screening for the separation of food waste from the waste stream.

A small-scale extruder hydraulic press (Orex Press®, [76]), operating at 200 bar, was used to reduce the food waste content from 5 – 20 wt.% in the MSW to less than 2 wt.% in the RDF. The RDF produced in this process, referred to as Extruder Fuel Fraction (EFF), was used in the study on the influence of food waste content on the fuel’s properties and combustion behaviour in Paper II.

![Figure 17](image-url)

*Figure 17. On the left, municipal solid waste (MSW) before extrusion (5.62 kg). On the right, dry extruder fuel fraction, EFF, (4.90 kg), a RDF suitable for combustion obtained after MSW extrusion in the Orex Press®.*

The chlorine, ash and energy contents of the FF/RDF and EFF described above are shown in Table 3.

**Mechanical Heat Treatment**

Mechanical Heat Treatments are technologies that combine mechanical processing and mild temperature heat treatment for conditioning waste fuels before they are incinerated [79]. Torrefaction of shredded and screened waste can be considered as one such process. It has gained attention in recent years since it significantly improves the properties of the biomass as fuel. Recently, torrefaction has also been applied to biomass waste streams such as demolition waste and construction wood and/or forest residues from woodcutting [80, 81], both torrefaction products presenting similar properties. Torrefaction is a mild thermal treatment, operating with a temperature range from 200 to 350 °C in a reducing atmosphere and with a residence time between a few minutes for large-scale operations to 2 hours for laboratory-scale operations.
Torrefaction yields three products: solids (hereinafter, referred as char), condensable gases and non-condensable gases. Char is the primary product and retains up to 90% of the energy content from the raw material and 70% of the mass. This char exhibits hydrophobic behaviour and improved grindability, making its storage and transportation easier compared to raw biomass. Using torrefaction, woody materials such as WW can be turned into a coal-like fuel which can be burnt in existing coal-fired power plants.

Torrefaction of DC wood and RDF was described in Paper IV, with an emphasis on the improvement of fuel properties by converting the fuels into a char, and an evaluation of PCDDs and PCDF formed during the process.

**Sampling and preparation of fuel blends**

Due to the inherent heterogeneity of the waste materials, a thorough sampling and blending procedure is needed to ensure the homogeneity of the fuel blends (Figure 18). For each individual material (DC, MSW, RDF and EFF), a standardized quartering procedure was carried out at the collecting sites, resulting in approximately 25 kg of representative sample of each material. Afterwards, materials were air-dried at 40 °C to constant weight to facilitate the next steps of grinding and homogenization. Metal and glass pieces were manually removed from the materials followed by homogenization. Next, materials were ground to ≤1 mm by using a cutting mill, and homogenized again. The material assigned for the combustion behaviour study (Paper II) underwent a second grinding, to reduce the size to ≤0.5 mm, and homogenization. Finally, materials were blended according to the ratios specified for each study and subsequently pelletized (6 mm diameter; 10 – 12 mm length) (Papers III – IV).

For Paper II, the household waste-based materials (MSW, RDF and EFF) were combined with DC or ST in different weight ratios to produce fuel blends. The ratios used were 80:20 (80% household waste:20% woody material), which was an attempt to produce a fuel with a blend ratio widely used for fuel production in co-combustion facilities, and 60:40, which was an attempt to produce a fuel blend with enhanced properties in terms of energy and POPs formation. For Papers III – IV, a 20:80 DC ratio was used instead.
Figure 18. Schematic of sampling and sample preparation for the waste and fuels described in Papers II – IV
5. THERMOCHEMICAL EXPERIMENTS

In this chapter, the experiments carried out, the set-ups and the analytical procedures used in this thesis are briefly summarized.

Combustion behaviour experiments

Thermal analysis 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. It has been used for analyzing the co-combustion of biomass and coal or lignin blends [87-93] and even MSW and coal blends [94]. The combustion behaviour of the different fuels was tested using a Stanton-Redcroft 625 Simultaneous Thermal Analyser (STA) which combines thermogravimetry (TG) and differential scanning calorimetry (DSC). About 2 – 4 mg of sample were heated from room temperature to 600 °C at 10 °C min\(^{-1}\) in an oxidative atmosphere (O\(_2\), 60 mL min\(^{-1}\)). The rate of weight loss, heat flux, temperature and time were simultaneously recorded. These data were used for calculation of TG, DTG (derivative of the TG curve), and DSC curves. Information about initial temperature (T\(_i\), “temperature where the rate of weight loss accelerates due to the onset of the combustion” [95]) and burnout temperature (T\(_{bo}\)) were determined graphically from these curves and used to provide a better understanding of the fuel’s combustion behaviour. Results for the combustion performance of the fuels are reported in Paper II.

Decomposition of fuels under pyrolytic conditions

A thermogravimetric analyser (Netzsch STA 409), coupled with a Fourier transform infrared spectrometer (Bruker EQUINOX-55), TG-FTIR, was used to study the decomposition of different fuels under pyrolytic conditions by analyzing the volatiles evolved during the process and the temperature range at which that took place (Paper II). Approximately 30 g of samples were heated from room temperature to 600 °C at 10 °C min\(^{-1}\) in an inert atmosphere (N\(_2\), 100 mL min\(^{-1}\)). Data on pyrolytic decomposition of fuels are reported in Paper II.
Emissions from combustion

*Domestic pellet stove*

DC wood and household waste fuels (MSW and RDF) were co-combusted in a domestic pellet stove as an intermediate evaluation stage prior to proceeding to larger-scale experiments (pilot-scale and/or demo-scale). Since a domestic pellet stove is easy to operate and designed to manage relatively low fuel feeding rates, it was an appropriate way to carry out combustion experiments.

The pellet stove used was an 11 kW EPE-01A (Haverland®) (*Figure 19*). Experiments were carried out at the University of Alicante (Spain). The stove consists of a top feed burner, an element which heats the first pellets for starting ignition, a combustion chamber with bottom and side holes forming combustion air inlets, an air inlet pipe and two fans, one which distributes the heated air into the room and a second which pushes the exhaust gases from the combustion chamber to a stainless steel stack. Heating power can be manually regulated by means of a room temperature set point. Fuel feed rate and heated air flow can also be regulated to achieve the desired room temperature. Further details of the stove are given in *Paper III*.

*Figure 19.* Domestic pellet stove used for the co-combustion experiments described in *Paper III*. 
Combustion runs

The combustion runs were divided into two stages. The first stage, lasting approximately 30 minutes, saw that the pellet stove started up and achieving a continuous feed of fuel corresponding to a chamber temperature between 220 and 380 °C. Afterwards, between 770 – 960 g of fuel, except for ST (550 g), were fed and burnt and the flue gas evolved sampled over approximately 60 minutes. During the combustion runs, the set point was manually regulated and always kept 2 degrees higher than the ambient temperature to ensure a continuous fuel feed and to force the stove to work in a continuous mode. Each material was tested in duplicate. Sampling blanks were prepared by allowing air to pass through the sampling train over 60 minutes without inserting the nozzle into the stack.

Flue gas sampling

The sampling set-up used for capturing the POPs (PAHs, PCBzs, PCPhs, PCBs, PCDDs and PCDFs) present in the flue gas from the co-combustion runs was based on the U.S. EPA method 23 A [96] with slight modifications to the absorbing solutions. A schematic of the sampling set-up is shown in Figure 20. The flue gas was removed from the sampling port in the stack with a probe and forced through a glass fiber filter and a solid absorbent to collect the POPs. Afterwards, the flue gas was bubbled through acidic and alkaline absorbing solutions to capture HCl [97]. The volume of gas sampled in each run varied between 0.99 and 1.33 Nm³.

Emission data from the co-combustion of waste-based fuels are described in detail in Paper III.

**Emissions from torrefaction**

**Tubular torrefaction reactor**

DC and household waste fuel torrefaction tests were carried out at the Swedish University of Agricultural Sciences (SLU, Umeå), in a stainless steel bench-scale tubular reactor (*Figure 21*) (length: 300 mm; diameter: 120 mm; volume: approximately 1 L) placed in a muffle furnace (ELF 11/6, Carbolite) [98, 99].

*Figure 21. Bench-scale tubular torrefaction reactor (Paper IV).*

**Torrefaction runs**

The aim of the torrefaction runs was to determine the concentration of PCDDs and PCDFs in the torrefaction flue gas (*Conf.1* set-up in *Figure 22*) from three different fuel blends. In addition, the fuel blend yielding the torrefaction flue gas with the highest PCDD and PCDF concentrations was selected for a second test where the torrefaction gas was combusted (*Conf.2* set-up in *Figure 22*) in order to simulate the afterburning of gas in full-scale torrefaction facilities.

Approximately 200 g of fuel were used in each *Conf.1* runs and 150 g in *Conf.2* runs. The operating conditions for torrefaction were the same for both types of experiments. To minimize the oxygen level, the sample inside the reactor was flushed with N₂ for approximately 30 minutes. Once the reactor was placed in the oven, the N₂ flow was reduced and pre-heated at 220 °C before reaching the reactor. Then, the fuel was pre-heated until it reached the torrefaction temperature, 220 °C. Hereinafter, this stage will be referred to as the *pre-heating stage*. It lasted 30 minutes. Once the temperature inside the reactor reached 220 °C, the set point of the furnace was manually controlled to maintain a steady 220 °C and avoid uncontrolled temperature increases due to exothermic reactions [99]. This stage will be referred to as the *torrefaction stage*. It lasted 60 minutes. For the *Conf.2* runs, the torrefaction gases leaving
the reactor were mixed with enough $O_2$ to ensure their complete combustion in a ceramic furnace at 900 °C. All materials were tested in triplicate and field blanks were prepared by passively exposing the sampler to the ambient atmosphere in the experimental area.

**Flue gas sampling**

The sampling set-up used for capturing the PCDDs and PCDFs in the flue gas from the torrefaction (Conf.1) and combusted torrefaction gas (Conf. 2) is shown in Figure 22. The flue gas leaving either the torrefaction reactor or the combustion furnace, depending on the set-up, was removed, cooled down and the condensable gases, if any, were collected in a round flask. The non-condensable gases were collected in a gas sampler which consisted of a glass fiber filter and polyurethane foam plug (PUF). In the Conf.1 set-up, PCDDs and PCDFs from the pre-heating and torrefaction stages were collected separately, while in the Conf.2 set-up, they were collected together. The outlet of the gas sampler was connected to a partial-vacuum pump to facilitate sampling.


The effects of using different waste-based fuels on the formation of PCDD and PCDF in both the torrefaction process itself, and in the combusted torrefaction gas, are reported in Paper IV.
Analysis of POPs: extraction, clean-up and instrumental analysis

As described before, two different types of POP samplers were used in this work: a glass fiber filter and a solid absorbent (Amberlite® XAD-2 resin) (Paper III) or PUFP (Paper IV). The POPs of interest were Soxhlet extracted from the sampler used for each sample, with 400 ml toluene over 24 hours. Prior to extraction, samplers were spiked with \(^{13}\)C-labelled internal standards for the target POPs. The extract was concentrated using rotary evaporation and divided into three aliquots (50:25:25), saving one of them (25%) as a backup sample.

For the determination of PCDDs, PCDFs (Papers III and IV) and PCBs (Paper IV), 50% of the concentrate extract was cleaned up (Figure 23) by applying it through a multilayer silica column followed by an alumina oxide column. Afterwards, fractionation was carried out in a column with AX-21 carbon and celite, resulting in one fraction containing PCDDs, PCDFs and planar-PCBs, and a second one containing the non-planar PCBs. For further purification, an additional multilayer silica column was used.

A 25% aliquot was used for PAH, PCBz and PCPh determination (Paper III). PCPhs were separated from PCBzs and PAHs by liquid-liquid extraction using 0.5 M NaOH. The aqueous phase containing the PCPhs was acetylated by adding acetic acid anhydride and extracted with cyclopentene. The organic phase containing PAHs and PCBzs was through a deactivated SiO\(_2\) column and eluted with cyclopentene.

Regardless of the target POPs, after the clean-up step, all the samples were concentrated and the corresponding \(^{13}\)C-labelled recovery standards were added prior to analysis. All the target compounds were analyzed using GC/HRMS with a Hewlett-Packard 5890 gas chromatograph (Agilent Technology) coupled to an Autospec Ultima mass spectrometer (Waters Corporation), using a DB-5ms J&W fused silica capillary column (60 m \(\times\) 0.25 mm i.d. x 0.25 \(\mu\)m film thickness).

The PCDD, PCDF and PCB analytes were quantified using the isotopic dilution method. Data with recoveries out of the acceptable ranges established by the EN 1948:1-3 standard [100] were not included.
Figure 23. Experimental clean-up procedure applied to POPs samplers for PCDD, PCDF, PCB, PAH, PCPh and PCBz determination (Papers III – IV).
6. THE EFFECT OF UPGRADING ON THE PERFORMANCE OF FUELS

As described in chapter 3, the presence of food waste in fuel produced for energy recovery affects the quality and increases the likelihood of the formation of chlorinated organic pollutants [57, 58] under specific conditions. In addition, parameters related to the combustion behaviour of a fuel, such as initial or burnout temperature, are not usually linear functions of the fuel composition [101]. These parameters affect the combustion performance of the fuel [87] and the efficiency of the process [87, 101]. For this reason, it is of great importance to evaluate the combustion behaviour of the fuels as a first step before using them in full-scale combustion facilities. The study for Paper II focused primarily on the effectiveness of two different mechanical treatments (shredding and screening and extrusion) to reduce food waste content from MSW, and how this reduction affects the combustion behaviour of the fuels when they are used in WtE processes.

Reduction of food waste content

As waste undergoes mechanical treatment, the waste components change to the extent that materials such as food waste cannot be easily identified or quantified. For that reason, for Paper II, two food waste-related parameters (easier to quantify than food waste content) were selected as indicators for assessing the effectiveness of food waste reduction by two mechanical treatments: chlorine content [55, 56] and lower heating value of the fuel [51]. Fuel samples were collected after the MSW (5 – 20 wt.% food waste) had been shredded and screened (RDF) (<5 wt.% food waste) or extruded in a high pressure press (EFF) (<2 wt.% food waste) (Table 3). Shredding and screening achieved both a greater reduction of chlorine (64%) and a higher increase in energy content (27%) than extrusion of the MSW (44% and 12%, respectively) (Figure 24). It was therefore concluded that shredding and screening is a more effective method for removing chlorine from MSW than extrusion. The reduction of chlorine and the increase in energy content of the fuel may indicate a reduction of the food waste content. However, as sources other than food waste may contribute to the chlorine content in the MSW [56], it is not possible to attribute this reduction solely to the food waste.
Figure 24. Comparison of the energy content (MJ kg\textsuperscript{-1}) and chlorine content (mg kg\textsuperscript{-1}) of the MSW and the fuels obtained after each mechanical treatment: shredding and screening or extrusion in a high pressure press. MSW: municipal solid waste; RDF: refuse-derived fuel; EFF: extruder fuel fraction.

**Effect of food waste content on combustion behaviour**

For Paper II, in order to evaluate the impact of the reduction in the food waste content of the household waste-based fuels on their combustion behaviour, MSW, RDF and EFF were tested using STA and the initial (T\textsubscript{i}) and burnout (T\textsubscript{bo}) temperature were graphically determined (Table 4). To facilitate the interpretation of the nature of each decomposition stage, the combustion behaviour of a reference biomass material, stemwood (ST) (Figure 25), and the thermal decomposition of EFF under pyrolytic conditions (Figure 27) were also studied using STA and TG-FTIR respectively.

Thermal oxidation of MSW, RDF and EFF revealed a very similar combustion behaviour occurring in three stages (Figure 26). The temperature ranges for each of the three decomposition stages were 200 – 260 °C, 260 – 375 °C and 375 – 500 °C respectively. The nature of each specific peak is explained below.
**Figure 25.** DSC profiles of the combustion of ST at 10 °C min\(^{-1}\). ST: stemwood pellets.

**Figure 26.** DSC profiles of the combustion of MSW, RDF and EFF at 10 °C min\(^{-1}\). MSW: municipal solid waste; RDF: refuse-derived fuel; EFF: extruder fuel fraction.
Of immediate interest when comparing the DSC profiles of ST and MSW-based fuels is the number of decomposition stages for each of them: two for ST and three for the MSW-based fuels. The first MSW-based fuel’s peak (200 – 260 °C) is absent from the DSC profile of the ST (Figure 25), suggesting a non-lignocellulosic nature for compounds decomposed during this stage. Comparison of the DSC profiles of the MSW-based fuels shows that when the food waste content of a fuel decreases (Table 4), this peak becomes more intense. If the food waste content decreases, the content of non-lignocellulosic materials such as plastics in the fuel increases. This fact supports the theory that the nature of this first peak can be attributed to the suggested non-lignocellulosic nature of compounds decomposed during this stage. In addition, the presence of non-lignocellulosic materials in the fuel seems to produce earlier decomposition of the fuel compared to ST (Figure 25), which is also shown by the \( T_i \) data (Table 4).

### Table 4. Food waste content, initial (\( T_i \)) and burnout temperature (\( T_{bo} \)) of each fuel. ST: stemwood (virgin biomass); MSW: municipal solid waste; RDF: refuse-derived fuel; EFF: extruder fuel fraction.

<table>
<thead>
<tr>
<th></th>
<th>ST</th>
<th>MSW(r)</th>
<th>RDF</th>
<th>EFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food waste(^1)</td>
<td>wt.%</td>
<td>0</td>
<td>5 – 20</td>
<td>&lt;5</td>
</tr>
<tr>
<td>( T_i )(^2)</td>
<td>°C</td>
<td>287</td>
<td>203</td>
<td>205</td>
</tr>
<tr>
<td>( T_{bo} )(^3)</td>
<td>°C</td>
<td>495</td>
<td>501</td>
<td>502</td>
</tr>
</tbody>
</table>

\(^1\)Food waste content; \(^2\)\( T_i \): initial temperature; \(^3\)\( T_{bo} \): burnout temperature

The nature of the second (260 – 375 °C) and third (375 – 500 °C) peaks can be interpreted based on the results from the TG-FTIR analysis of the EFF under pyrolytic conditions (Figure 27). The first peak in the TG-FTIR (336 °C) is due to the release of carbon dioxide, aldehydes, ketones and carboxylic acids which are all products of the decomposition of lignocellulosic materials (paper, cardboard or wood). The major products of decomposition in the second peak (474 °C) are long chain aliphatic compounds suggesting the decomposition of synthetic polymers. Therefore, the second and third peaks in the combustion of EFF (331 °C and 461 °C) correspond to the oxidation of the volatiles released during the pyrolysis of lignocellulosic and synthetic polymers respectively. The broadness of the third peak (461 °C) is probably related to the oxidation of the char produced in the second stage when the pyrolysis of the lignocellulosic materials takes place. This observation is also valid for MSW and RDF. In addition, comparison of the three MSW-based DSC profiles clearly shows that when the food waste content of a fuel increases (Table 4), the second peak shifts to
lower temperatures, suggesting that the presence of food waste accelerates the decomposition of the fuels, something also supported by the T\textsubscript{i} data (Table 4).

Figure 27. TG-FTIR analysis of EFF (extruder fuel fraction): (a) two dimensional representation of the pyrolysis (Absorbency vs. wavenumber); (b) FTIR spectra for volatiles produced at 336 °C and 474 °C (Temperature vs. wavenumber) and (c) kinetic traces of the major FTIR absorption peaks (Absorbency vs. Temperature). A.U.: Absorbance units.

At this point, it seems that two factors determine the acceleration of the decomposition of the fuels: (i) the presence of plastics, the effect of which is clearly observed when the DSC profiles and T\textsubscript{i} of MSW-based fuels and ST are compared (Figures 25 and 26, Table 4), and (ii) the presence of higher amounts of food waste in the fuel, also supported by the T\textsubscript{i} data (Table 4). If plastics were the only component in the fuels responsible for the shift in the MSW-based fuels’ DSC curves to lower temperatures, then those fuels with higher plastic content would have a lower T\textsubscript{i}. However, the fuel with the lowest T\textsubscript{i} is the one with lowest plastic content (MSW). For this reason, the main conclusion of Paper II was that the acceleration of the decomposition of the MSW-based fuels may be due to a combined effect of the food waste and plastics present in the fuel.

Previous studies have reported an acceleration in the thermal decomposition of some materials due to the presence of either PVC [102, 103] or impurities that easily decompose [101]. However, this is the first study that provides clear observations of the three-stage oxidation decomposition of MSW-based
fuels and in which food waste is also considered to play an important role in combination with the presence of plastics.

Fuel blends, combinations of MSW, RDF or EFF with virgin wood (ST) or demolition and construction (DC) wood, were also studied for Paper II to discover whether an interaction may exist between the different materials and the effect on their combustion behaviour [87]. The acceleration of the thermal decomposition of the fuels due to the presence of non-lignocellulosic materials and food waste was also clearly observed in the fuel blends.
7. HOW DOES FUEL UPGRADING AFFECT THE POP EMISSIONS?

Current WtE plants are designed to maximize destruction of the waste and energy recovery while minimizing the formation of pollutants. The application of the best available techniques, together with the introduction of restrictive environmental laws, have led to a drastic decrease in the emissions of POPs into the environment [16]. However, continual development is required in order to achieve the lowest impact possible on the environment from the incineration plants.

The formation of POPs depends on many factors. In particular, PCDD and PCDF formation depends on combustion and post-combustion zone temperatures, residence time and turbulence in the combustion zone. As mentioned in chapters 2 and 3, the waste fuel composition is also an important factor. It is desirable to reduce the availability of those elements such as active catalysts that play an important role in the formation of pollutants and are present in the waste fuel. The study in Paper I highlighted the importance of applied specific pre-treatment techniques to reduce the amount of contaminants which are involved in the formation of toxic emissions from combustion of WW. The study in Paper II found that the chlorine content in the waste fuels decreased when mechanical pre-treatments such as shredding and screening or extrusion were used with MSW. The influence of the waste pre-treatments on the combustion behaviour of a fuel was also researched for Paper II, and it was found that the combination of food waste and plastics in the fuel accelerates its thermal decomposition. The next step in these studies is to evaluate whether these changes in the waste fuel composition and combustion behaviour have an influence on the formation of POPs. Paper III describes a follow-up study which addresses the question of whether decreasing the food waste content in waste fuel by means of using waste pre-treatments is a good method of reducing POP emissions from incineration.

Two different fuel blends, prepared by combining demolition and construction (DC) wood with MSW (5–20 wt.% food waste content) or RDF (<5 wt.% food waste content) in an 80:20 ratio by weight (DC:MSW and DC:RDF), were selected for carrying out the combustion tests detailed in Paper III. In addition, a ST fuel as well as ST:MSW and ST:RDF fuel blends
were also tested to study the impact of the degree of contamination of the WW on the formation of POPs.

**Effect of food waste content on POP emissions**

The total food waste content was 4 wt.% for the MSW-based and 1 wt.% for the RDF-based fuel blends tested for **Paper III**. Comparison of ST-based and DC-based fuel blends showed that the presence of MSW or RDF in them had no effect on total PAH emissions (**Figure 28**). The average PCBz emissions from DC:RDF were higher than for DC:MSW, 260 and 170 μg kg\textsuperscript{-1}fuel\textsuperscript{-1} respectively (**Figure 29**), but no clear effect was observed for the ST-based fuel blends. There was no clear evidence of variation in the PCPh emissions with food waste content in any of the fuel blends (**Figure 29**), indicating that food waste content is not influential in the formation of these pollutants. Once again, this trend was observed for the formation of both total and toxic PCBs (**Figure 30**). In contrast, the use of either MSW or RDF in a fuel blend seemed to affect the total PCDD and PCDF emissions from the DC-based fuels, but not the toxic PCBs (**Figure 31**).

**Figure 28.** Total PAH emissions expressed as the sum of the Naphthalene (yellow) and the total PAH emissions excluding naphthalene (grey) (mg kg\textsuperscript{-1}fuel\textsuperscript{-1}) of the fuels tested. #1 and #2 stands for replicate 1 and 2 of each fuel blend respectively. ST: stemwood; MSW: municipal solid waste; RDF: refuse-derived fuel. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste.
**Figure 29.** Total PCBz (grey bar) and PCPh (blue bar) emissions ($\mu g$ kg$_{fuel}^{-1}$) of the fuels tested. #1 and #2 stand for replicate 1 and 2 of each fuel blend respectively. ST: stemwood; MSW: municipal solid waste; RDF: refuse-derived fuel. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste.

**Figure 30.** Total PCB emissions (blue bar) ($\mu g$ kg$_{fuel}^{-1}$) and PCBs TEQ emissions (grey bar) (ng WHO2005-TEQ kg$_{fuel}^{-1}$) of the fuels tested. #1 and #2 stand for replicate 1 and 2 of each fuel blend respectively. ST: stemwood; MSW: municipal solid waste; RDF: refuse-derived fuel; EFF: extruder fuel fraction. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste.
HOW DOES FUEL UPGRADING AFFECT THE POPs EMISSIONS?

Figure 31 Total PCDD and PCDF emissions (µg kg<sub>fuel</sub>) and PCDD and PCDF TEQ emissions (ng WHO<sub>2005</sub>-TEQ kg<sub>fuel</sub>) of the fuels tested. #1 and #2 stands for replicate 1 and 2 of each fuel respectively. ST: stemwood; MSW: municipal solid waste; RDF: refuse-derived fuel. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste.

In summary, the study described in Paper III found that the variation of the food waste content in the fuel blends seemed not to be a determining factor for the formation of PAH, PCBz, PCPh, PCB and toxic PCB, PCDD and PCDF emissions. Therefore, the composition of the lignocellulosic material (i.e. ST or DC) appears to be the main factor responsible for the variation in the POP emissions from the combustion of the fuels tested.

Effect of the degree of contamination of WW

The almost-zero effect of the variation of the food waste content in the fuel blends on the formation of POP emissions changed the focus of the study described in Paper III from the food waste to the WW component of the fuel blends. The presence of DC wood instead of ST in the fuel blends led to an increase of the emissions of all the POPs evaluated for Paper III, except PAHs. The PCBz concentrations increased more than 3 times (Figure 29). The PCPh emissions increased by 85% for the MSW blends and 233% for the RDF blends (Figure 29). A slight increase in the total PCB emissions was observed (Figure 30) from 7.2 µg kg<sub>fuel</sub> to 10.6 ± 2.4 µg kg<sub>fuel</sub> for ST-based and DC-based fuels respectively, while the PCDD and PCDF emissions (Figure 31) increased dramatically. The toxic PCDD, PCDF and PCB emissions clearly
followed the same trend (*Figure 30 and 31*). Conversely, the PAH emissions from ST-based fuels (*Figure 28*) were exceptionally high (32 ± 3.8 mg kg\textsuperscript{-1} fuel) compared to the other fuel blends. This increase can be attributed to low combustion efficiency when ST is combusted, which is reinforced by the high CO emissions (*Table 5*). Naphthalene represented the main PAH species in all the samples analyzed, contributing for up to 50% of the PAH emissions (*Figure 28*). Several studies have identified naphthalene as the main species out of the 16 EPA PAHs [46] formed during the combustion of woody materials [104, 105].

*Table 5. Energy content and chlorine, iron and copper content, density and combustion-related parameters of the fuels tested. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste.*

<table>
<thead>
<tr>
<th></th>
<th>ST</th>
<th>ST:MSW</th>
<th>ST:RDF</th>
<th>DC:MSW</th>
<th>DC:RDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHV\textsuperscript{1}</td>
<td>MJ kg\textsuperscript{-1}</td>
<td>19.0</td>
<td>18.8</td>
<td>19.8</td>
<td>18.6</td>
</tr>
<tr>
<td>Cl</td>
<td>%ds</td>
<td>&lt;0.01</td>
<td>0.21</td>
<td>0.10</td>
<td>0.47</td>
</tr>
<tr>
<td>Fe</td>
<td>mg kg\textsuperscript{-1}</td>
<td>10</td>
<td>720</td>
<td>302</td>
<td>1770</td>
</tr>
<tr>
<td>Cu</td>
<td>mg kg\textsuperscript{-1}</td>
<td>0.97</td>
<td>91</td>
<td>7.3</td>
<td>108</td>
</tr>
<tr>
<td>Density</td>
<td>kg m\textsuperscript{-3}</td>
<td>2760</td>
<td>1163</td>
<td>1322</td>
<td>1086</td>
</tr>
</tbody>
</table>

Combustion Parameters

- **Replicates**
  - #1
  - #2
  - #1
  - #2
- **Feed rate** kg h\textsuperscript{-1}
  - 0.55
  - 0.51
  - 0.73
  - 0.83
- **Flue gas sampled** Nm\textsuperscript{3}
  - 1.3
  - 0.99
  - 1.2
  - 1.2
- **CO** ppm
  - 1080
  - 983
  - 879
  - 754
- **NO** ppm
  - 3.3
  - 3.5
  - 10
  - 6.8
- **NOx** ppm
  - 6.7
  - 3.5
  - 11
  - 7.0
- **SO\textsubscript{2}** ppm
  - 2.4
  - 0.60
  - 0.24
  - 0.60
- **HCl** mg Nm\textsuperscript{3}
  - 0.17
  - 0.32
  - 6.3
  - 6.1
- **Cl\textsubscript{2}** mg Nm\textsuperscript{3}
  - 0.90
  - 4.1
  - 0.53
  - 0.70

ST: stemwood; DC: demolition and construction wood; MSW: municipal solid waste with 5 to 20 wt.% food waste content; RDF: refuse-derived fuel with up to 5 wt.% of food waste content. \textsuperscript{1}LHV: lower heating value; ds: dry sample.

The above results indicate that DC wood is the key factor in the formation of POP pollutants from the combustion process. There are a few factors related to the composition of the fuel blends and their potential to increase the POP emissions. One of them is, of course, the increase in the levels of chlorine available in the fuel blend (0.27% in DC wood versus <0.01% in ST – *Table 3*)). The most important source of organic chlorine in DC wood may be PVC residues from pipes, window frames and wall and floor coverings [23, 69]. The second factor may be the presence of PCP-treated timber in the DC wood source [106] which is a precursor for the formation of PCDDs and PCDFs. This idea is supported by the high levels of PCP (1700 μg kg\textsuperscript{-1} fuel) detected in DC wood used in this study. Another important factor is the presence of metals such as copper or iron in DC wood. Both are active catalytic metals that promote the formation of PCDDs and PCDFs [107]. Copper may originate...
from CCA-treated wood [69] while iron probably originates from metal scraps, coatings or paint [104].

In summary, the study described in Paper III found that the variation of food waste in the fuel blends, or in other words, the use of upgraded fuel (RDF) instead of MSW does not have a clear influence on the formation of PAH, PCBz, PCPh, total PCB and toxic PCB, PCDD and PCDF emissions. The use of DC wood is clearly related to the formation of POPs, in particular with toxic PCDDs, PCDFs and PCBs. Its large potential for promoting the formation of these pollutants may be related to the presence of plastics such as PVC, CCA-treated and PCP-treated wood in the source. In the light of the results described in Paper III, it seems reasonable to advise that further pre-treatment of DC wood be carried out before it is used as fuel in WtE plants, in order to mitigate environmentally hazardous emissions. This links back to Paper I, the WW composition case study, where it was shown that there is a need to assess the pre-treatment technologies currently applied to DC waste. It seems necessary to use and/or combine different mechanical treatments technologies with i.e. heat treatments in order to minimize the negative effect of the waste fuel composition on POP emissions.
8. TORREFACTION FOR MITIGATION OF POP EMISSIONS?

Biomass upgrading by torrefaction has been extensively studied [80, 83-85, 108-110] showing that such a process improves the energy content and quality of fuel produced from the biomass. A question that may arise is whether it is feasible to apply torrefaction to non-lignocellulosic material such as household waste: Is it possible to produce waste fuels for WtE plants with a high quality and a low potential for formation of toxic emissions by using torrefaction on waste streams instead of/or combining with mechanical treatments? However, it is not enough to produce sustainable, high quality, waste fuel. In addition, all the stages involved in the “fuel’s lifecycle”, from waste collection to combustion of the waste fuels in the WtE plants, need to have as low an impact as possible on the environment. Therefore, this also applies to the production process/upgrading of a fuel itself, in this case, torrefaction. Paper IV describes the need for studying whether torrefaction can enhance the quality of waste fuels and could contribute to a reduction in their emissions when they are combusted in WtE processes. Lastly, Paper IV describes studies into the impact of the torrefaction process itself in terms of toxic emissions.

The high levels of POPs formed from the combustion of the DC:MSW and DC:RDF fuel blends detailed in Paper III suggested the need for studying, as described in Paper IV, how technologies such as torrefaction could be used for these fuels to reduce their emissions when they are combusted in WtE plants. In addition, in the study described in Paper IV, a third fuel blend, ST:RDF, was used as a reference fuel blend because of its substantially lower ash and metal content. Comparison between these three fuel blends allows a study of the impact of using different types of MSW-based materials or virgin wood instead of DC wood on the torrefaction products.
Performance of the fuel blends and properties of chars

The char yields of the fuel blends tested for Paper IV were 89.3%, 84.5% and 85.7% for ST:RDF, DC:MSW and DC:RDF respectively, which still lies within the typical 80 – 90 % char yield associated with biomass torrefaction [99, 108, 111]. The energy content of the chars increased slightly (Figure 32) while the chlorine content was reduced compared to the fuels, which is also consistent with the results obtained from torrefaction of biomass [112]. Although DC:RDF showed a large reduction in chlorine content (56%) from 4200 to 1850 ± 130 mg kg\textsubscript{fuel}\textsuperscript{-1}, its chlorine content is still three times higher than that of the reference fuel (ST:RDF, 570 ± 60 mg kg\textsubscript{fuel}\textsuperscript{-1}). The chlorine reduction indicates the migration of chlorine from the fuels to the condensable and non-condensable gases. The chars, if used as fuel in WtE plants, may thus have a reduced potential for formation of chlorinated organic pollutants compared to the fuel blends.

![Figure 32. Comparison of the energy content (MJ kg\textsubscript{ds}) and chlorine, iron and copper content (mg kg\textsubscript{ds}) of the fuel blends and the chars. ST: stemwood; DC: demolition and construction wood; MSW: municipal solid waste; RDF: refuse-derived fuel. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste. (ds: dry sample)](image-url)
Fate of chemical contaminants

The importance of the chemical contaminants in DC wood (Paper I) and the variation in the composition of the waste fuels has been highlighted and discussed in previous chapters in this thesis. Trace metals such as Cu and Fe are well known to be highly efficient catalysts in the formation of PCDDs and PCDFs [19, 21, 22]. These two trace metals remained in the char at the torrefaction temperature (225 °C), the temperature at which tests were carried out for Paper IV (Table 6, Figure 32), but in particular, the Fe levels were surprisingly high i.e. 1400 and 4330 ± 1700 mg kg\textsubscript{fuel}\textsuperscript{-1} in the DC:RDF fuel blend and char respectively. This sharp variation may be attributed to the inherent variation in the fuel. Other trace metals such as Pb, Zn, As and Cr are among those considered as DC wood chemical contaminants. The study in Paper IV found that that most of these elements remained in the char (Table 6) with the exception of Hg. The relatively large standard deviation in char for Cu, Zn and, in particular, Pb content may be attributed in some way to the inherent heterogeneous composition of the DC wood [23, 60, 61].

Table 6. Trace metal content (mg kg\textsubscript{ds}\textsuperscript{-1}) of the fuel blends (feedstock) and the chars. ST: stemwood; MSW: municipal solid waste; RDF: refuse-derived fuel. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste. (ds: dry sample).

<table>
<thead>
<tr>
<th>mg kg\textsubscript{ds}\textsuperscript{-1}</th>
<th>ST:RDF</th>
<th>DC:MSW</th>
<th>DC:RDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content change ratio</td>
<td>1.12</td>
<td>1.10</td>
<td>1.22</td>
</tr>
<tr>
<td>Fe</td>
<td>300</td>
<td>630 ± 160</td>
<td>1770</td>
</tr>
<tr>
<td>As</td>
<td>0.18</td>
<td>0.21 ± 0.02</td>
<td>6.9</td>
</tr>
<tr>
<td>Cd</td>
<td>0.11</td>
<td>0.12 ± 0.01</td>
<td>0.64</td>
</tr>
<tr>
<td>Cr</td>
<td>8.2</td>
<td>7.9 ± 0.6</td>
<td>66</td>
</tr>
<tr>
<td>Cu</td>
<td>7.3</td>
<td>8.1 ± 0.7</td>
<td>110</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.22</td>
</tr>
<tr>
<td>Ni</td>
<td>1.3</td>
<td>1.6 ± 0.6</td>
<td>8.5</td>
</tr>
<tr>
<td>Pb</td>
<td>1.6</td>
<td>2.9 ± 1.1</td>
<td>260</td>
</tr>
<tr>
<td>Zn</td>
<td>35</td>
<td>46 ± 7.0</td>
<td>470</td>
</tr>
</tbody>
</table>

*ds: dry sample; figures in italics for Hg indicate that one or more replicates were below detection*

Our observations indicated that it might be possible to use torrefaction as a way of separating chlorine, which partially migrates to the gas phase, from elements such as iron or copper which are known to promote the formation of PCDDs and PCDFs. Torrefaction would therefore reduce the potential for PCDD and PCDF formation with regards to chlorine content, but increased amounts of catalytic elements in the char may still promote this formation during combustion.
Assessment of the PCDD and PCDF emissions from torrefaction

The PCDD and PCDF concentrations were assessed in the gas obtained from the torrefaction of the three fuel blends to evaluate the possible impact of the torrefaction process itself on toxic emissions. There were three main findings of this study, included in the Paper IV. The first is that higher PCDD and PCDF concentrations were present in the torrefaction gas than in the gas collected during the pre-heating stage (Figure 33). This indicates that the formation of PCDDs and PCDFs is more likely to occur during the torrefaction stage than the pre-heating stage. The second is the sharp increase in PCDD and PCDF concentrations when ST was substituted by DC wood, from 0.94 ng kg\textsubscript{fuel\(^{-1}\)} in ST:RDF to 1370 ± 310 ng kg\textsubscript{fuel\(^{-1}\)} in DC:RDF (Figure 33). The use of DC wood instead of ST in the fuel blend promoted PCDD and PCDF formation. This sharp increase may be related to DC’s high chlorine copper and iron content (Figure 32, Table 6). The third finding was that there were lower PCDD and PCDF concentrations produced from DC:MSW (250 ng kg\textsubscript{fuel\(^{-1}\)}) than from DC:RDF (1370 ± 310 ng kg\textsubscript{fuel\(^{-1}\)}). The lower environmental impact that MSW may have when combined with DC compared to RDF, along with its lower production costs, MSW does not need any further pre-treatment, support the idea of using MSW as feedstock for refinement by torrefaction.

Figure 33. PCDD and PCDF (ng kg\textsubscript{fuel\(^{-1}\)}) in the gas obtained during pre-heating and torrefaction of each fuel blend. ST: stemwood; MSW: municipal solid waste; RDF: refuse-derived fuel. Fuel blends ratio: 80 wt.% waste wood and 20 wt.% household waste.
Data for torrefaction of WW are scarce and, hence, comparison of various materials is difficult. Results detailed in Paper IV are only comparable with the PCDD and PCDF concentrations reported by Gao et al. [99]: 210 and 318 ng kg\textsuperscript{-1}\textsubscript{fuel}, for flue gas, during torrefaction of impregnated wood and particle board, respectively. These values are the same order of magnitude as the PCDD and PCDF concentrations in the DC:MSW torrefaction gas (250 ng kg\textsuperscript{-1}\textsubscript{fuel}).

The exceptionally high levels of PCDD and PCDF in the DC:RDF torrefaction gas highlighted the need for further study of it. For that reason, this fuel was selected for the final study described in Paper IV, to simulate the afterburner in torrefaction plants. Due to its high calorific value (5.3 – 16.2 MJ Nm\textsuperscript{3}) [113], the torrefaction gas is suitable for combustion. Therefore, it is commonly combusted in torrefaction processes to recover heat [114] before being emitted. The combustion of the DC:RDF torrefaction gas reduced the total PCDD and PCDF levels from 1370 ± 310 ng kg\textsuperscript{-1}\textsubscript{fuel} to 6.0 ± 5.8 ng kg\textsuperscript{-1}\textsubscript{fuel}. In terms of WHO2005-TEQ PCDD/F concentrations, the emissions were 0.060 ± 0.03 ng TEQ kg\textsuperscript{-1}\textsubscript{fuel}. It is of scientific interest to compare the toxic PCDD and PCDF emissions in the afterburner gas with those of gases emitted from other waste pre-treatment processes to understand the potential environmental impact. For example, the TEQ\textsubscript{PCDD/F} concentration from drying highly contaminated PCP-treated wood was 10 ng TEQ kg\textsuperscript{-1}\textsubscript{fuel} [115], which is considerably higher than the TEQ\textsubscript{PCDD/F} concentration from the afterburner gas. These observations indicated that the environmental impact of the torrefaction of waste upgrading to fuel may be quite low with regards to PCDD and PCDF emissions.

The study described in Paper IV found that torrefaction applied to MSW combined with DC wood produced a fuel with improved properties, lower PCDD and PCDF emissions from the process and lower production costs compared to RDF. Torrefaction seems to be a sustainable technology for improving the fuel properties of waste streams due to its lesser environmental impact regarding PCDD and PCDF compared to other waste pre-treatment techniques.

The quality of the waste fuels in respect of e.g. energy content is equally important in exhibiting as low potential as possible for the formation of toxic emissions from combustion. These emissions must meet limit values established by the legislation in order to mitigate their impact on the environment. For that reason, chars obtained from this study should be tested in combustion equipments/facilities and their emissions assessed before drawing any firm conclusions about their suitability of being used as fuel in WtE plants.
9. CONCLUSIONS AND FUTURE WORK

The major conclusions of this thesis could contribute to the production of high quality waste fuels with a lower potential to form pollutants when used in WtE processes, implying a mitigation of their impact on the environment.

The study of the variation of the contaminants in domestic and imported waste wood (WW) fuel samples, Paper I, confirmed a high variability in their composition. Results from this study highlighted the importance of characterizing WW fuel composition especially given the current globalization of the WW market. This case study also revealed that screening alone is not an effective method for reducing those chemical contaminants with the potential for POP emission from the WW source. On the other hand, screening and shredding appeared to be more effective methods than extrusion in terms of removing chlorine from household waste-based fuels, thus lowering the potential formation of POPs when such fuel is used with WtE technology.

The evaluation of the combustion behaviour of the waste fuels in Paper II revealed, for the first time, a three-stage oxidative decomposition of MSW-based fuels. In addition, an acceleration of the decomposition of MSW-based fuels (blends) compared to lignocellulosic fuels was observed, which may be due to the presence of plastics and food waste in the fuels (blends).

Results from Paper III revealed that the variation of the food waste content (1 – 4 wt.%) in the fuels seemed not to be a controlling factor for the formation of PAHs, PCBzs, PCPhs, PCBs and toxic PCDDs, PCDFs and PCBs. On the contrary, WW, in particular DC wood, seemed to be the key factor for the formation of all these pollutants except PAHs. This was probably due to the presence of chemical and material contaminants (i.e. PVC, CCA-treated and PCP-treated WW and scraps of metals).

Torrefaction seemed to be a sustainable treatment for converting waste streams to fuel due to its low PCDD and PCDF emissions (Paper IV). Torrefaction of DC:MSW yielded a char with enhanced properties as a fuel, low PCDD and PCDF emissions from the process and low costs associated with the production of the fuel. The use of DC waste wood instead of clean
Several of the studies in this thesis indicated the importance of the composition of the contaminated WW in the formation of POPs during thermal treatments. There is an urgent need to assess the WW contamination regularly and adapt the pre-treatment technologies to minimize the environmentally hazardous emissions without compromising the quality of the fuel. Reduction of food waste content in the MSW has to be seen as a way of obtaining a resource for the production of renewable energy such as biogas, compost or fertilizer, but not as a practice for minimizing the toxic emissions from thermal processes. Torrefaction seems to be a sustainable alternative to mechanical waste pre-treatments.

**Future work**

While carrying out the studies that formed this thesis, it was noticed that there was a lack of available data regarding the composition of household waste. A study of individual components (e.g specific types of plastics) that comprise current MSW would produce a better understanding of the combustion behaviour and performance of the fuels when used for WtE. In addition, there is also a lack of data about the composition of WW, based on the country of origin. This knowledge could be used to forecast the composition of the WW fuel consumed in WtE plants, and allow selection of specific waste pre-treatments with the aim of minimizing emissions into the environment.

Further research should be focused on torrefaction as a pre-treatment technique to enhance the properties of the waste fuels. It would be of great interest to optimize the torrefaction temperature and fuel composition (including blend ratios) to maximize the char yields and the quality of the fuels. A valuable follow-up study would be to investigate the combustion of the chars to evaluate the toxic emissions. The aim would be to compare the toxic emissions and fuel properties of the waste fuels (produced by means of different waste pre-treatments) and their chars in order to determine the suitability of each waste pre-treatment for producing quality waste fuels. Finally, the most promising fuels should be subjected to full-scale tests to verify the results obtained in the laboratory.

It could also be of interest to study whether the acceleration of the decomposition of the fuels due to the presence of plastics and food waste observed in Paper II is present when combusting chars.
ACKNOWLEDGMENTS

First of all, I would like to thank my supervisor Stina Jansson for giving me this opportunity. It has been a great pleasure to work with you. Thanks for your valuable advice, for being always available and for your enthusiasm. I am also grateful to Per-Erik Persson for all the interesting and inspiring discussions and for the great time I spent working with him in Västerås. Thanks to my assistant supervisors Erik Björn and Michael Finell for their guidance. I am deeply grateful to my co-authors Vitaliy Budarin, Núria Ortuño, Ignacio Aracil, Juan Conesa, Nils Skoglund and Qiuju Gao. I have learnt a lot from all of you! I would like to thank VafabMiljö Kommunalförbund and the Umeå University Industrial Doctoral School (IDS) for their financial support. Thanks to Vattenfall for generously sharing their data and Carl Nordensköld and Christer Forsberg for their valuable comments. Thanks to Henrik Antti and Jerker Fick for their advice during the annual evaluations. Thanks to all of you who have made this thesis happen.

Thanks to all my MKL colleagues for their nice company during the lunches, Friday’s fika, knitting clubs… MKL is such a nice working environment!! Thanks Per, Maria and Anna for your help in the lab, and Lisa for being always willing to help. Special thanks goes to the always-full-of-energy Sandra who has literally been close to me from the first day! (And Joao, of course!). Obrigada! Thanks to Matyas, my taco buffet soul mate; Ivan and his sense of humor; Mandana (and her cows) and Mehdi for their kindness; Christine, merci for visiting our sofa ☺; Kristine for the delicious toast Hawaii; Jana, my favourite vegan neighbour; Cathrin for her sweetness; Eva for her “combustion” help, Lan, Jin Darya, Marcus, Majid, Aleks and Malin. I wish you all the best!!!

What a great idea to put three completely different personalities (according to the MBTI® personality test) in the same office! Seriously Qiuju (😊), thanks for bringing equal calm and meanness to our office!! And thanks Mirva for letting me break your bubble every now and then (and break into ICA Mirva)! Both of you have been the greatest support over these years!! IDS has also been an important part of this thesis. Thanks Anna, Benkt and
Petter for creating this inspiring environment, and thanks to Ellis, Diana, Kristina, Mattias, Markus, Daniel, Bea and Niklas for their support but also for the laughs and the red pants! Lycka till!

Thanks to all my colleagues at VafabMiljö for their kindness and the English! Especialmente a Melissa, ¡pura energía colombiana!

Thanks to my favourite photographer Ellis; we have done so many things together!! Gracias Diana por esa alegría y buena energía que irradias. Thanks to my friend Mustang, sorry, Hendrik for being such great (Skype) company. Thanks Carina and Thomas for the great time at your place. I miss those dinners! Gracias a Maria por los buenos ratos en Umeå, and Mireille for the loooong walks. I wish you all the best my friends!

Es hora de agradecer a la gente de casa: Mil gracias a mi amiga Laura por eso, ¡por ser la mejor amiga! A mi amiga Carmen por estar siempre dispuesta a escuchar a quien lo necesita. A Esther M., Edurne, Bábara Toni y Andrés por estar siempre “conectados” para charrar un rato; y al resto de Terreta Connection, mi Núri, Patricia, Blanca y Pinturs por encontrar siempre un ratito para vernos cuando vuelvo a casa. A Juan Carlos y a Fabián, ¡gracias por la visita!; y a mis tíos Pepe y Angustias por su cariño y por esa manta de patchwork que me abriga en las frías tardes de sofá en Umeå.

Por último, gracias a mi hermana por estar siempre a mi lado. ¡No te imaginas cuanto he aprendido de ti! Gracias a André por traer un poco de calma a esta familia de locos, y a la pequeña Zoe por sus besos y sus “ciao” que me dejan siempre con una sonrisa.

Y esta tesis termina como empezó, dedicada a mis padres, quienes con tanto amor y apoyo, habéis hecho que estando lejos os sintiera más cerca que nunca. Os quiero.

“Y si no necesitáis ninguna cosita más de mí, se despide…”

F.A.
REFERENCES


7. Avfall Sverige (The Swedish Waste Management Association), *Kartläggning av sammansättningsanalyser på svenskt hushållsavfall (Mapping of compositional analyses of Swedish household waste)*. 2016 (under publication).


32. Gao, Q., Dioxins and dioxin-like compounds in thermochemical conversion of biomass: formation, distribution and fingerprints, in Department of Chemistry. 2016, Umeå University.


REFERENCES


REFERENCES


REFERENCES


67. Energy Center of Nehterlands (ECN), Phyllis2, database for biomass and waste. 2015, Energy Center of the Netherlands.


72. Department of Environmental Food & Rural Affairs (DEFRA), Mechanical Biological Treatment of Municipal Solid Waste 2013.

73. Department of Environmental Food & Rural Affairs (DEFRA), Mechanical Heat Treatment of Municipal Solid Waste 2013.


technologies, in 3rd International Conference on Sustainable Solid Waste Management. 2015.


REFERENCES


100. European Committee for Standarization (CEN), Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs. Part 1: Sampling of PCDDs/PCDFs; Part 2: Extraction and clean-up of PCDDs/PCDFs; Part 3: Identification and quantification of PCDDs/PCDFs; Part 4: Sampling and analysis of dioxin-like PCBs. 2006.


106. Jenkins, B.M., Jones, A.D., Turn, S.Q., and Williams, R.B., Emission Factors for Polycyclic Aromatic Hydrocarbons from Biomass
REFERENCES


“And when it’s done, it’s done”
Anonymous student