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Carbon materials: towards a circular economy through thermochemical recycling of mixed waste

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Abstract

Carbon materials, such as paper, wood, plastic and textiles, play an important role in our everyday life, from clothes and packaging to infrastructure. However, the use of those materials follows a linear way. We take carbon resources, we make products, and we discharge them in a short amount of time, producing GHG emissions along its supply chain. From its extraction, manufacture and, unlike other materials, also at its end of life, releasing its embedded carbon into the ecosphere.

One approach to reduce emissions and resource extraction is to move towards a circular economy, by recirculating waste to produce new materials. However, today's material recycling process fall short, only a small fraction is recycled and often to a lower quality. As an alternative, this work shows that emphasizing carbon recovery, instead of material recovery, changes the perspective on carbon-containing waste flows.

Consequently, material flow analysis of the current carbon material system was set, illustrating that the system losses are greater than the carbon material produced. If those carbon losses are assumed to be released as CO_2, they will equal 6% of the current GHG. The flow analysis also showed that there is enough carbon in the waste for producing synthetic materials and that carbon can help to reduce the emissions and decouple from fossil extraction.

This analysis also displayed that the carbon available in post-consumer waste consists of a mix of synthetic and natural carbon materials, together with heteroatoms such as oxygen, nitrogen, and chlorine. A potential way to recover all carbon is thermochemical recycling, which can break down materials into building blocks, similar to the chemicals employed in the petrochemical industry. As mixed waste comprises a wide variety of materials, the thermal conversion poses a variety of challenges ranging from the unknown product distribution to the fate of heteroatoms.

The thermochemical conversion of three different mixed wastes was tested in a pilot-scale reactor to understand the product distribution. The experimental results showed that the conversion yielded a mixture of gases and aromatics compounds, together with a high share of unconverted. While some of these products can be used directly, such as olefins and benzene, others require further recovery and processing. Another finding is that a higher conversion temperature helps to limit heteroatoms in the hydrocarbons. Increasing the temperature to 800°C reduced the Chlorine-content in aromatics under ppm levels, but Oxygen and Nitrogen content are higher than ppm level and that may affect the carbon recovery and may require further separation steps.

While thermochemical recycling has the potential to go towards a circular economy and reduce emissions, further efforts are required to tackle the different challenges to make thermochemical conversion a viable recycling method for mixed wastes.

Keywords: carbon materials, circular economy, mixed waste, recycling, thermochemical

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List of publications

This thesis is based on the following papers, referred to in the text according to their designated Roman numerals for main author and alphabetical for co-author. The contribution for each manuscript is described using CRediT (Contributor Roles Taxonomy).

Publications included

Paper I

I. Cañete Vela, T. Berdugo Vilches, G. Berndes, F. Johnsson, H. Thunman
Co-recycling of natural and synthetic carbon materials for a sustainable circular economy
CRediT: Methodology, data curation, formal analysis, validation, visualisation, writing – original draft.
Under review.

Paper II

I. Cañete Vela, J. Maric, J. González Arias, M. Seemann
Conversion of non-recyclable cable plastic residue into valuable feedstock via steam gasification
CRediT: Conceptualisation, formal analysis, investigation, validation, visualisation, writing – original draft.
To be submitted.

Paper A

H. Thunman, T. Berdugo Vilches, M. Seemann, J. Maric, I. Cañete Vela, S. Pissot, H.N.T. Nguyen
Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery
Sustainable Materials and Technologies. 22 (2019)
CRediT**:** Investigation**,** data curation, writing – review & editing of the introduction and validation of the carbon flows.

Paper B

S. Pissot, T. Berdugo Vilches, J. Maric, I. Cañete Vela, H. Thunman, M. Seemann
Thermochemical Recycling of Automotive Shredder Residue by Chemical-Looping Gasification Using the Generated Ash as Oxygen Carrier
Energy & Fuels. 33 (2019) 11552–11566.
CRediT: Experimental investigation, data curation, writing – review & editing

Publications not included

I. Cañete Vela, J. Maric, M. Seemann
Valorisation of textile waste via steam gasification in a fluidised bed reactor
Heraklion 2019 – 7th International conference on sustainable solid waste management
CRediT: Conceptualisation, formal analysis, investigation, validation, visualisation, funding acquisition, writing – original draft.

J. Maric, T. Berdugo Vilches, S. Pissot, I. Cañete Vela, M. Gyllenhammar, M. Seemann
Emissions of dioxins and furans during steam gasification of Automotive Shredder residue; experiences from the Chalmers 2–4-MW indirect gasifier
Waste Management. 102 (2020) 114-121
CRediT: Experimental investigation, data curation, writing – review & editing

I. Staničić, I. Cañete Vela, R. Backman, J. Maric, Yu Cao, T. Mattisson
Fate of Lead, Copper and Zinc during Chemical Looping Gasification of Automotive Shredder Residue
Fuel. 302, 15 October 2021, 121147
CRediT: Resources, Conceptualisation, Investigation, writing – review & editing.

Shouzhuang Li, I. Cañete Vela, M. Järvinen, M. Seemann
Polyethylene Terephthalate (PET) recycling via gasification – The effect of operating conditions on product distributions
Waste Management. 130, 1 July 2021, 117-126
CRediT: Investigation, formal analysis, supervision, writing – review & editing.

I. Cañete Vela, J. Maric, S. Pissot, M. Seemann
Thermochemical recycling of Automobile Shredder Residue in DFB gasifier
The International Symposium on Feedstock Recycling of Polymeric Materials (ISFR) 2019
CRediT: Conceptualisation, formal analysis, investigation, validation, visualisation, writing – original draft.

List of Abbreviations

ABS: Acrylonitrile Butadiene Styrene
ASR: Automotive Shredder Residue
BTX: Benzene, Toluene and Xylene
CCU: Carbon Capture and Utilisation
CE: Circular Economy
C-Material: carbon material
CP: cable plastic
CRtM: Carbon Resources to Material
daf: dry ash-free
DFB: Dual fluidised bed
FC: Fixed Carbon
GC: Gas chromatograph
GC-MS: Gas chromatograph - Mass spectrometer
GHG: Green House Gas
HTR: High-temperature reactor
HVC: High-Value Chemical
MtC: Million ton Carbon
MtEco: Material to Ecosphere
MtEn: Material to Energy
PA: Polyamides
PAH: Polyaromatic hydrocarbon
PAN: Polyacrylonitriles
PBT: Polybutylene terephthalate
PC: Polycarbonate
PE: Polyethylene
PET: Polyethylene terephthalate
PEX: Cross-linked Polyethylene
PMMA: Polymethyl methacrylate
PP: Polypropylene
PS: Polystyrene
PUR: Polyurethane
PVC: Polyvinyl chloride
P&C: Paper and Cardboard
SPA: Solid-phase adsorption
TGA: Thermogravimetric analysis
TX: Textiles

"Nothing in life is to be feared; it is only to be understood."

- Marie Skłodowska Curie

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Figures and tables

Background

A linear way: take, make, waste

Along with population expansion and economic development has come increased consumption of materials to meet societal demands for housing and infrastructure, nutrition, healthcare, mobility, communication, services, and consumer products. In Year 2017, the global material footprint was 100.6 Gigatonnes (Gt), of which 92 Gt were extracted resources, and 8.6 Gt were cycled material that re-entered the economic system. The system is mainly linear (take, make, waste) with only 8.5% (in mass terms) cycled, without considering composition, quality level, or if the cycled material becomes a product[1,2].

In the next 40 years, the global consumption level of biomass, fossil fuels, metals and minerals are expected to double[2], while annual waste generation is projected to increase by 70% by year 2050[3]. Thus, progression towards a circular use of materials is essential. Carbon resource consumption must be carefully considered because it creates major environmental challenges, such as resource depletion, waste generation, and greenhouse gas (GHG) emissions that contribute to climate change.

Carbon-based fuels account for about 90% of the current global primary energy supply. While energy use is the leading contributor to anthropogenic GHG emissions, and decarbonisation of the energy system is essential to limit the global temperature increase to 1.5°C[4], the production and use of carbon-based materials (C-Materials) entail significant GHG emissions[5]. The emissions from C-Materials have two sources: direct emissions from energy production, and embedded[1] carbon emissions. The latter are estimated to represent two-thirds of the carbon footprint for synthetic products6, and they are most relevant at the end-of-life because their embedded carbon can be released as CO_2. While it is possible to decarbonise the energy system using renewable energy sources such as wind and solar, the amount of carbon required for a product remains the same. Therefore, to achieve deep reductions in carbon emissions beyond decarbonisation of the energy supply, it is essential to eliminate the emissions linked to C-Materials.

C-Materials produce carbon emissions during carbon resource extraction; during the transformative production processes; and at the end-of-life owing to incineration or degradation in nature or landfills. However, these emissions are considered differently for synthetic and natural C-Materials. Biomass-based products, such as wood, paper and natural textiles, are often considered CO_2 neutral regardless of their end-of-life treatment. It is usually stated that biomass takes up CO_2 and offsets the emissions from its incineration[6,7], although the carbon neutrality of biomass depends on the forest/land management practices, type of biomass feedstocks and the timeframe analysed[8,9].

[1] *Also called Material-retained carbon.*

Biomass is also considered a substitute for fossil-based products, such as plastics and synthetic fibres. Not only is biomass not always carbon-neutral, but also the biomass supply is limited due to resource constraints and trade-offs with sustainability[10]. For example, cropland expansion may cause deforestation, with consequent GHG emissions and negative impacts on biodiversity[11] and competition with food, water and land uses. Thus, there is a need for sustainable treatment of C-Materials.

The concept of the circular economy is way to tackle the unsustainable use of C-Materials. C-Material waste recirculation to produce new materials prevents embedded carbon emissions at the end of life and can reduce resource use. A widespread misconception is that recycled material displaces primary production on a one for-one basis[12]. Indeed, not all the waste that is cycled today can become a new product, and it is often the case that products manufactured from waste are of a lower quality than the original[13–15], which means that the cycled material do not always replace virgin resources[16–18]. Ideally, the use of natural resources should be minimised. Likewise, the demand for carbon products should be covered to the greatest extent possible by keeping all the carbon in a circular loop, such that is recirculated indefinitely, with minimum losses to the environment in the forms of emissions and material waste.

Current recycling and its limitations

While the importance of circular economy for achieving net-zero emissions is currently a topic of vigorous debate[6,7,15,19–22], the challenges related to recycling are sometimes neglected[15]. The main challenge is the quality of the recycled material since it determines the functionality and ability to be properly recovered. The possibility to achieve 100% recycling is constrained by the efficiency of collection, sorting and by reprocessing capacity[15,23–25], and is further limited by the degradation of the material during the use phase and manufacture process.

Most recycled materials are of lower quality than the original product[23], as depicted in Figure 1. For instance, recycled paper pulp is more commonly used for newsprint and packaging. As these usually require lower paper grades, and every time it is recycled, the fibre quality degrades. Ultimately, the fibre becomes un-usable for material purposes[13]. In the case of timber, it is possible to convert wood to a secondary use within particleboard. Afterwards, the particleboard may be recycled one or more times into new generations of particleboard[14], finally leading to its disposal. Another example is cotton, which can be recovered as an artificial cellulosic fibre, although this does not have the same properties as cotton and cannot be recycled[26]. Similarly, mechanical recycling of plastics is associated with material downgrading[15]. For example, polyethylene (PE) packaging is recycled for blowing moulding applications for lower-quality products[27].

A small fraction of plastic is manufactured back into products of similar quality. Polyethylene terephthalate (PET) bottles are made from equivalent grades of plastics. As a result, PET bottles of high quality can be manufactured via solvolysis and mechanical recycling[28]. Nevertheless, both of these processes require high-purity material without dyes or other contaminants.

Therefore, approximately 80% of the PET bottles are reprocessed to polyester fibres[15,28]. The current processes can recycle single-stream plastics, although it remains challenging to recycle mechanically contaminated plastics.

When the plastic waste is mixed, it is necessary to separate, wash, and prepare it for recycling[29]. These physical transformations are essential to producing a clean and homogeneous product that is mechanically recycled. Even when the plastics are treated, not all the plastics are suitable for material recycling, e.g., thermosets and composite materials. Examples of blended materials are beverage cartons and textiles (e.g., polycotton). As depicted in Figure 1, these materials are composed of both synthetic polymers and natural C-Materials. For both products, functionality, as a barrier to or enforcement of extended durability, dictates the choice of material, rather than the end-of-life considerations.

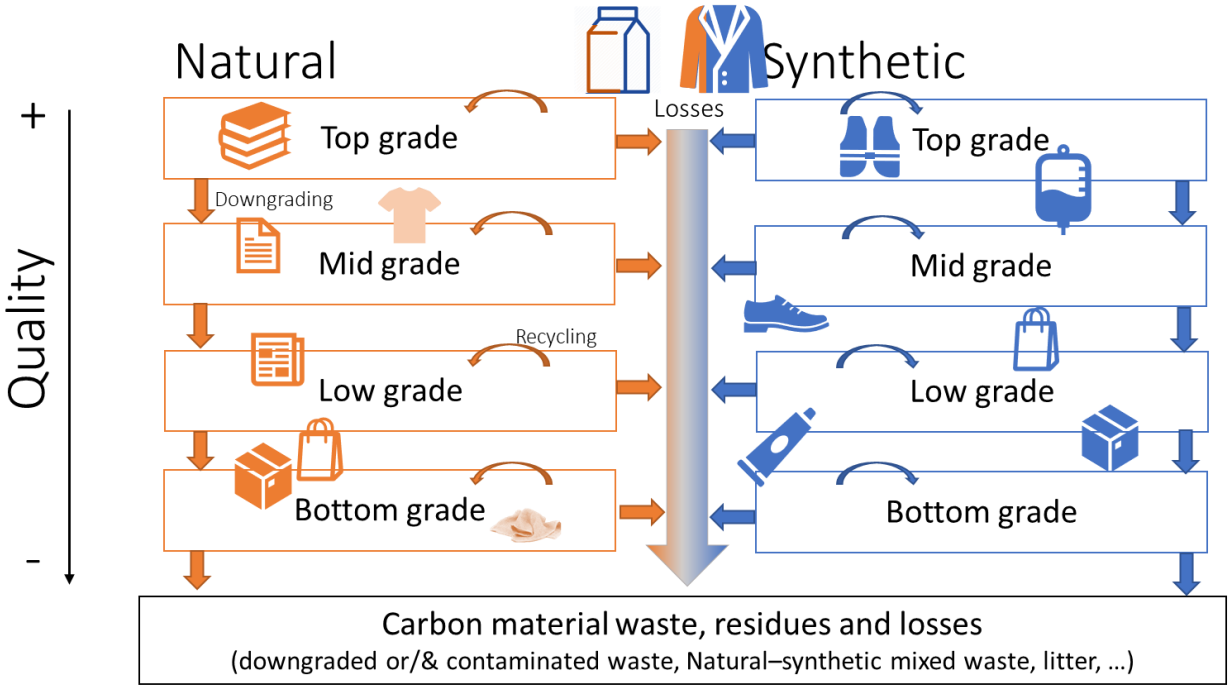


Figure 1. Cascade effect of the recycling of natural and synthetic C-Materials.

Given the current limitations of material recycling, C-Materials mostly follow a linear scheme. Wood products are scarcely recycled[14,30], and <5% of plastic waste becomes a new product[24,29,31–33]. Paper products are the most recycled carbon materials; ≥40% of new paper products come from recycled pulp manufacturing[13,34]. The C-Materials that are most-commonly recycled today are single-stream flows, such as paper/paperboard, polyolefins, and PET[13,14,29]. However, many waste streams are a mixture of different polymers. This mismatch between heterogeneity and applied technologies creates a large share of highly blended polymer mixtures, which cannot be recycled with reasonable separation and sorting effort and/or be recycled into high-quality products via material recycling.

When material recycling is not used, disposal and incineration with or without energy recovery are employed as end of life treatments. This approach goes against the notion circularity if the fossil carbon is emitted as CO_2 without further recovery[25]. Carbon dioxide capture and utilisation (CCU) has been proposed to avoid those emissions, as well as to provide a carbon source for the production of C-Materials[6,7,35], although high levels of hydrogen and energy must be expended[36]. Thermochemical (or feedstock) recycling, which breaks down polymers into their constituent monomers or building blocks, is suitable as a feedstock source for the petrochemical industry. As the chemical structure of the material is partially preserved, thermochemical recycling can be positioned between material recycling and CCU, requiring less energy than the latter.

As summarised in Table 1, thermochemical processes can be separated into pyrolysis and gasification. Pyrolysis aims to produce monomers and liquids; polymer decomposition occurs in the absence of oxygen and often requires low-to-medium temperatures. Gasification converts C-Materials into gaseous products at higher temperatures and under partial oxidation conditions.

Table 1. Summary of the characteristics of thermochemical recycling processes and Carbon Capture and Utilisation (CCU).

	Process	**Characteristics**	**Waste types**	**Output**
Thermochemical	Pyrolysis	Low-temperature (500°–700°C) absent of oxygen	PMMA, PS	Monomers: MMA (98% at 450°C), Styrene (61% at 515°C) [37]
		Medium-temperature (500°–700°C) absent of oxygen	Single or mixed PO	Gas, liquid and wax products (C_1–C_{50}) [37]
	Gasification	High-temperature (600°–900°C) partial oxygen	Single/mixed / biomass	High gas yield (H_2, CO, CH_4, olefins and aromatics)
CCU	Combustion	Combustion + hydrogenation	Mixed	CO_2 + H_2 (which needs to be synthesised into chemicals)

Of these processes, pyrolysis is preferable from the thermodynamic point of view, as it preserves the structures of the existing molecules. However, the direct formation of valuable monomers depends on the nature and composition of the feedstock applied. This route corresponds to the traditional naphtha/alkane cracking process that is currently used to produce monomers, mostly olefins, from fossil fuels. Some polymer streams are exemplified in Table 1, showing that the optimal temperature for monomer recycling depends on the waste type, as is the case for Polymethyl methacrylate (PMMA) and Polystyrene (PS). Pyrolysis of polyolefinic plastics can also be optimised to produce ethylene and propylene or liquid fuels[22,38–41].

Gasification is less feedstock-dependent and is suitable for treating highly heterogeneous blends[42–44]. Several thermochemical recycling processes are currently in the application or demonstration phase[45]. For instance, the Enerkem biofuels plant converts 0.1 Mt/year of dry mixed municipal waste into 38,000 Nm^3 of methanol and ethanol[46], which can be used as a feedstock in the petrochemical industry. In this plant, only 30% of the weight is recovered as product, entailing carbon losses. These losses restrict closing of the loop and can conceivably end up as carbon emissions. While thermochemical recycling can be performed with higher efficiency, the potential recycling of mixed waste via thermochemical methods needs to be explored in more detail, including its limitations and implications within a circular economy. It is essential to devise a framework within which this technology is feasible and achieves net-zero emissions.

Aim: Towards a circular economy for C-Materials

A transition from the take, make, waste model to a circular one is needed to reduce resource consumption, emissions and waste generation. A sustainable future comes from having a close the loop approach and also considering net-zero carbon emissions. Progression towards circularly using C-Materials requires technologies that treat any waste, single-stream or mixed, and produce products of the same or higher quality as the original. Such technologies would aid in the transition from a linear to a circular use of C-Materials, such that fraction that currently ends up in energy recovery or disposal becomes the feedstock for new products.

Thermochemical recycling provides an opportunity to close the C-Material cycles by returning non-recyclable carbon waste and rest fractions into products of high quality, while reducing resource use and waste generation, and avoiding CO_2 emissions at the same time.

While thermochemical recycling technologies hold promise with respect to mixed carbon waste, to support their industrial implementation, there needs to be more knowledge regarding the technologies and the carbon material flows. In this context, understanding the C-Material fractions and gaining insights into their heterogeneity are vital to optimise and comprehend thermochemical recycling.

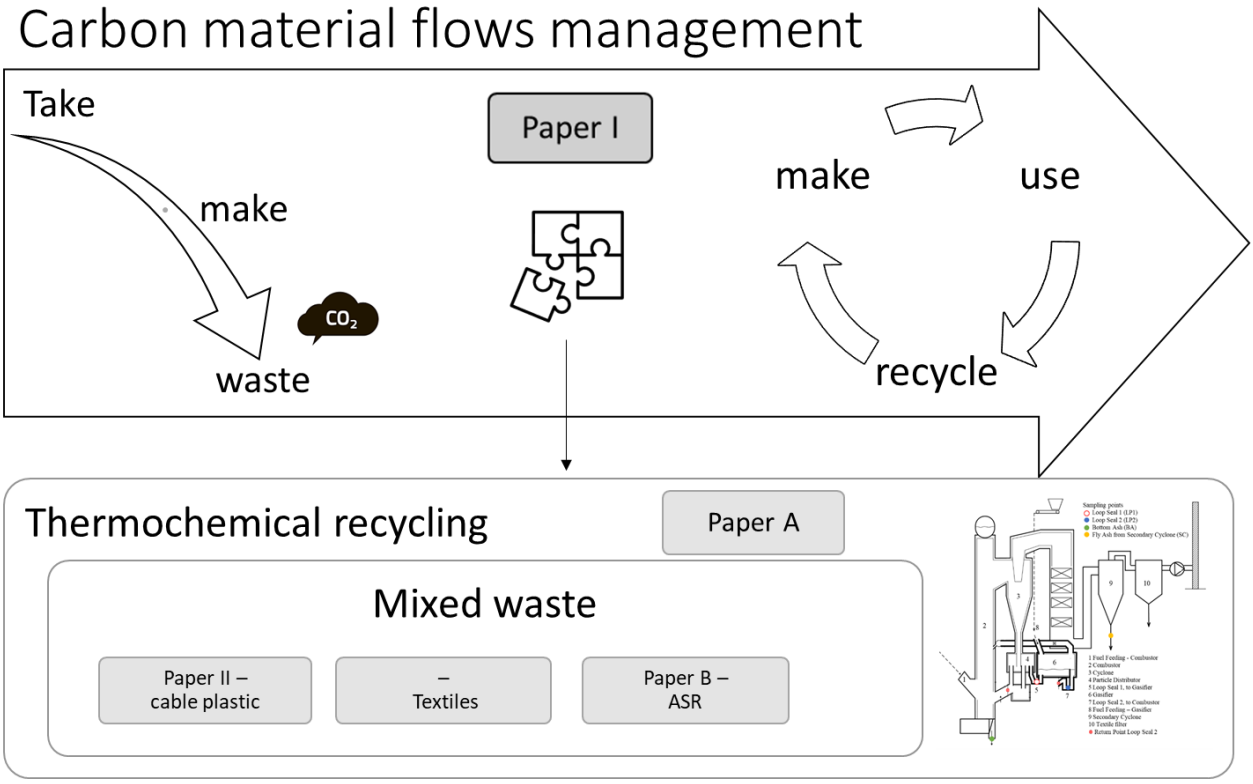


Figure 2. The two parts of this work: C-Material flows management; and thermochemical recycling of mixed waste: cable plastic, textile and Automotive Shredder Residue (ASR).

This work illustrates the possibilities and challenges of thermochemical recycling of mixed carbon materials for a circular economy and net-zero emissions society. The thesis approaches the problem on two levels: a system perspective investigating the management of global C-Material flows; and an applied investigation on thermochemical recycling of mixed waste on a semi-industrial-scale plant (Figure 2).

The first part aims to build a framework around C-Materials flows, exploring how large the flows are and which types of materials they contain. Three research questions are posed to gain an understanding of how to move from a take-make-waste model towards a circular and net-zero emissions economy:

Question 1: How does the global carbon material system look today?

Question 2: What is needed to achieve a circular economy and net-zero emissions (in the carbon material system)?

Question 3: Which flows and materials are available for thermochemical recycling?

Material flow analysis was used to answer these research questions, as described in *Paper I* (*Co-recycling natural and synthetic carbon materials for a sustainable circular economy*).

The second part focuses on the thermochemical recycling of C-Materials and is a compilation of *Paper II* and *Papers A* and *B*. Two questions were asked to assess the theoretical and practical possibilities and challenges of thermochemical recycling of mixed carbon waste:

Question 4: Which products can be theoretically obtained from thermochemical recycling of mixed carbon waste?

Question 5: Which products are obtained from mixed waste processing in a pilot-scale reactor?

The theoretical possibilities regarding thermochemical recycling of mixed waste were derived from *Paper A* (*Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery*). The findings from experimental campaigns conducted in the Chalmers semi-industrial plant are summarised to answer Question 5, presenting the results from the gasification of three mixed wastes.

The gasification test results are collected from *Paper II* (*Conversion of non-recyclable cable plastic residue into valuable feedstock via steam gasification)* for cable plastic waste, *Paper B (Thermochemical Recycling of Automotive Shredder Residue by Chemical-Looping Gasification Using the Generated Ash as Oxygen Carrier)* for Automotive Shedder Residue, and non-published data for the textile waste.

Finally, a summary of the results and future perspectives on achieving carbon circularity are presented in the final chapter, identifying future research directions.

How to make carbon materials circular

Carbon materials today

Nowadays, the production and use of C-Materials entail significant waste generation, resource use and carbon emissions. The C-Materials emissions arise from energy production and embedded carbon. While it is possible to decarbonise the energy system using renewable energy sources, the amount of carbon required for a product will remain. In 2018, about 1.8 Gt of biomass and fossil fuels were extracted to produce 1.3 Gt of C-Material-containing products, excluding the resources used for energy generation (*Paper I*). About 0.8 Gt of these products became waste the same year, with less than 40%$_w$ being recycled.

Even if all waste is sent for recycling, the current recycling methods cannot maintain a complete cycle, due to losses and low-quality recycled materials. For instance, from the 430 Mt of synthetic C-Materials produced in 2018, about 70% became waste[33]. Assuming that all plastic recycling is done via existing methods, which can recover 60%-70% of the material[23], we still maintain more than half of current oil consumption. Employing only current recycling techniques ensures a linear pathway, and the high levels of resource consumption, residue generation, and emissions remain. Thus, a new approach is needed towards achieving a circular and net-zero economy.

A material flow analysis is set up for the current worldwide C-Materials system to explore how to achieve this target. The system includes global flows of paper, cardboard, wood, plastics, and fibres, which together account for all processes from carbon resource extraction to end of life. The flows are described in terms of carbon mass (millions of tonnes of carbon, MtC), to unveil how much carbon there is in the materials and where the carbon losses occur.

A global dataset of C-Material products for 2018 is used to construct the C-Materials system (*Paper I*). The material flow analysis excludes energy and comprises three processes: Extraction, Manufacture, and Use. Extraction refers to mining fossil resources or harvesting biomass for material production, which is linked to the generation of unused materials, here referred to as Carbon Resource to Material Losses (CRtM-Losses). The extracted fossil fuels, oil and natural gas are converted to high-value chemicals (HVCs). The Manufacture process involves all the transformation steps from extracted materials to synthetic and natural C-Materials. During this process, there is generation of by-products and waste, which are not used for material production (CRtM-Losses). These flows are either used for energy generation (Material to Energy, MtEn) or simply lost or emitted (Material to Ecosphere, MtEco). The Manufacture process can also assimilate unused C-Materials from the Use process, such as plastic or paperboard wastes. The Use process consists of the use and end-of-life phase, including C-Materials that are kept in use (often called ‘stock’) and post-consumer waste that can be used for energy recovery (MtEn) or that is lost to final disposal (MtEco). In addition, the residues can be recirculated back to the industry for recycling.

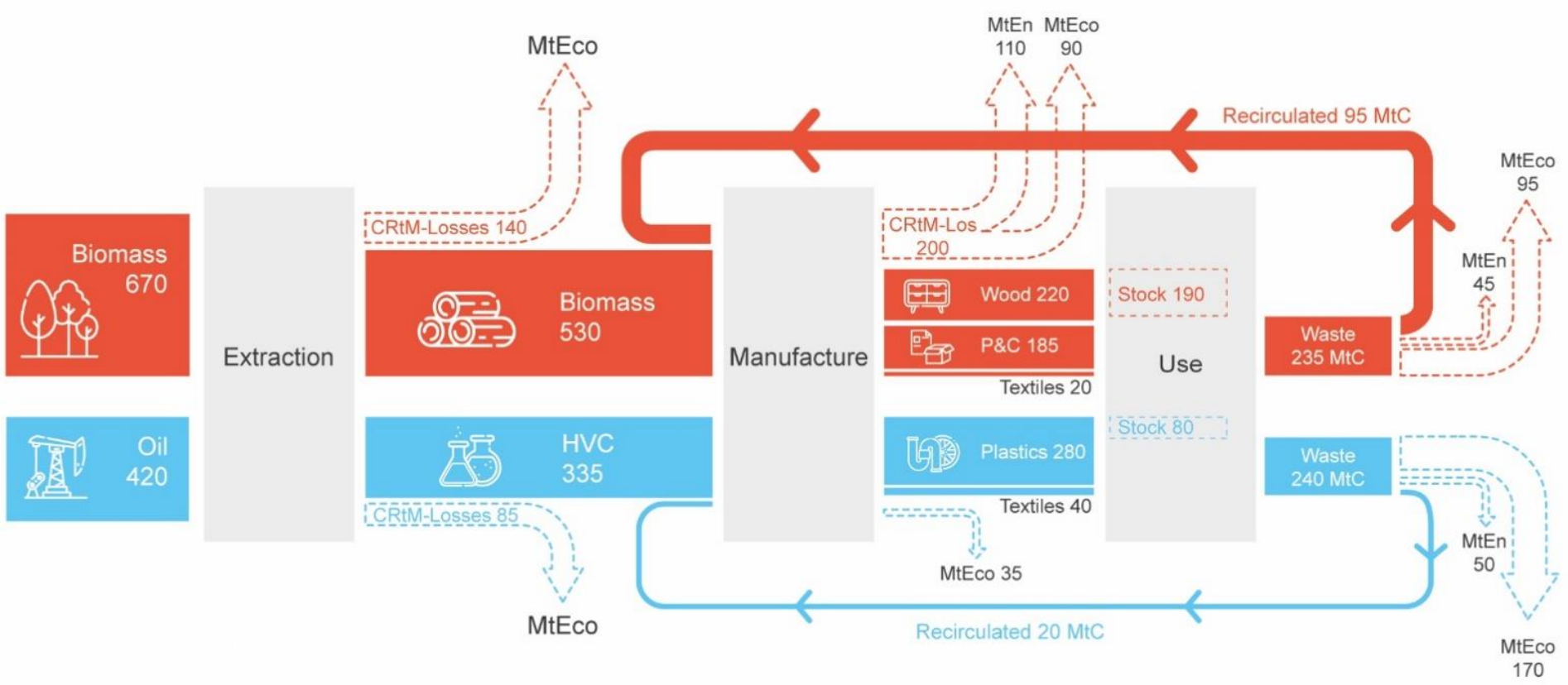


Figure 1. Current C-material system (Paper I)

CRtM-Losses: Carbon Resource to Material Losses, MtEn: material to energy, MtEco: material to the ecosphere, HVC: High Value Chemicals, P&C: paper & cardboard

Figure 3 shows the global C-Materials system for year 2018. The carbon material system is divided into two main C-Material types: natural carbon materials such as wood, paper, textiles like cotton; and synthetic C-Materials such as plastics (also referred to as synthetic polymers) and synthetic fabrics. Figure 3 also includes the resources and process losses for manufacturing these products, excluding the resources needed for energy.

The amount of carbon extracted to produce C-Materials was about 1,090 MtC in 2018, consisting of fossil and biogenic resources. Of the 420 MtC of oil extracted, 85 MtC were lost during the transformation processes to produce the base chemical needed for plastic production. The base chemical here consists of methanol and HVC, including ethylene, propylene and aromatics. Of the 670 MtC of biomass harvested, 530 MtC were used for material production, and 140 MtC remained in the forest as logging losses/primary residues.

In addition to the 225 MtC of CRtM-Losses experienced during extraction, 230 MtC were lost during the Manufacture process, representing about 200 MtC of losses in natural C-Materials and 35 MtC of losses in synthetic C-Materials. Of the natural C-Material losses, 110 MtC were sent to energy production (MtEn), mainly to the pulp and paper industry to meet internal process energy needs and some as wood by-products used as fuels. The remaining 90 MtC were lost to the environment (MtEco).

The amount of carbon in all the C-Materials manufactured globally was about 745 MtC. Approximately 425 MtC were in natural C-Materials, including 220 MtC in wood products, 185 MtC in paper and cardboard products, and 20 MtC in natural textiles. The remaining 320 MtC were in synthetic C-Materials, mainly plastics (280 MtC), and 40 MtC in synthetic fibres. Most C-Materials reach the end of life the same year, producing a large amount of waste.

The post-consumer waste was estimated at 475 MtC with similar natural and synthetic materials shares. 235 MtC were a post-consumer waste of natural C-Materials, of which 45 MtC were incinerated with energy recovery, and 95 MtC were recirculated to produce new C-Materials. The remaining 95 MtC were lost to the environment (MtEco). For synthetic materials, the post-consumer waste was 240 MtC, and most wastes ended up as MtEco (170 MtC), followed by MtEn (50 MtC), and only 20 MtC were recirculated back to the Manufacture process, yielding approximately 15 MtC of synthetic products. Almost all the recycled synthetic C-Materials ended up in lower-quality products, with only 2% found in materials of quality similar to that of the original material[33,47].

It is evident that the use and production of C-Materials come with losses. About 815 MtC were lost from the carbon material system, which is greater than the total amount of C-Materials produced. Two observations can be extracted from the material flow analysis: (1) assuming that all the carbon ends up as CO_2, about 3 $GtCO_2$ are released from this system, which is equivalent to 6% of GHG emissions including land use[48]; (2) the carbon available in waste alone is greater than the carbon needed for synthetic C-Materials production.

Towards carbon circularity

Figure 4 depicts a proposed scenario in which the post-consumer waste carbon is recirculated to produce plastics, so as to avoid emissions, as well as to promote decoupling from fossil fuel use and the utilisation of waste. In total, 355 MtC of waste are recirculated to produce synthetic C-Materials, with 20 MtC being used in the existing mechanical recycling, and 335 MtC undergoing thermochemical recycling to produce the base chemicals needed to make synthetic C-Materials. In contrast, the natural C-Materials part of the system remains unaffected in the scenario proposed here.

Under these conditions, the total losses decrease from 815 MtC to 395 MtC. Assuming again that the carbon ends up as CO_2, the emissions will decrease by half, by approximately 1.5 $GtCO_2$, or 3% of global emissions. These discharges consist almost exclusively of bio-based carbon, which with appropriate management practices, can be considered carbon-neutral. Another important aspect is that the system is decoupled from the fossil resources used to produce synthetic materials. The proposed scenario also avoids the current extraction of about 420 MtC of fossil resources, reduces resource consumption, and decreases the associated CRtM-Losses by 85 MtC.

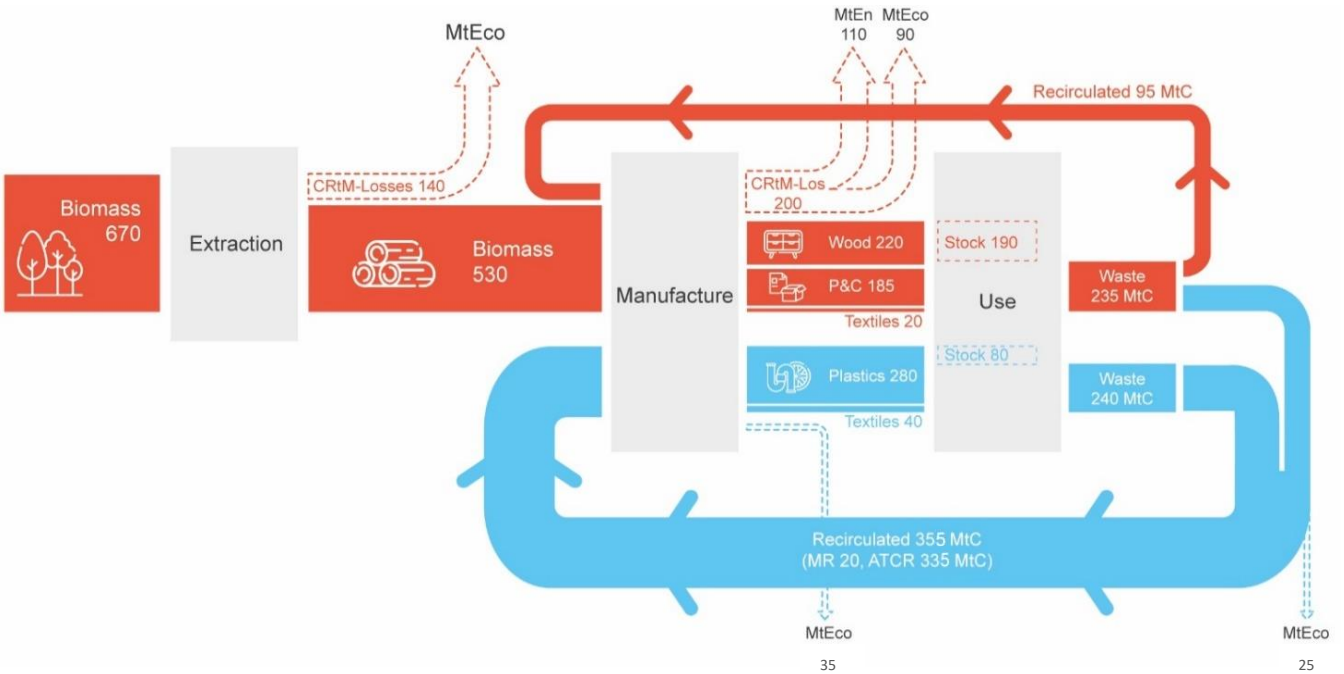


Figure 4. Flow-chart for the proposed recirculation of waste for a circular C-Material system.
CRtM-Losses: Carbon Resource to Material Losses, MtEn: material to energy, MtEco: material to the ecosphere, P&C: paper & cardboard, MR: Mechanical recycling, ATCR: Advanced thermochemical recycling

The post-consumer waste replaces the current fossil feedstock to produce the base chemicals. Despite the complexity of the chemical sector, only seven primary chemicals: ethylene and propylene, referred to as light olefins (220 MtC); benzene, toluene, and mixed xylenes, referred to as BTX (100 MtC); methanol (35 MtC); and ammonia (185 Mt), constitute the crucial building blocks of the chemical industry[5]. While ammonia is mainly used for fertilisers, light olefins and aromatics are collectively termed HVCs and are the main building blocks for synthetic C-

Materials. In addition, a small fraction (approximately 15 MtC) of the methanol is used for plastics, plywood, and textiles.

Thus, the necessary amount of carbon is approximately 335 MtC, and thermochemical recycling should provide a route towards HVCs and methanol. Table 2 shows a summary of the available post-consumer flows and their thermochemical characteristics. For the scenario presented, the post-consumer waste will consist roughly of 19%$_w$ wood, 23%$_w$ Paper and cardboard (P&C), 5%$_w$ natural textiles, 9%$_w$ synthetic textiles, and 44%$_w$ plastics. It should be noted that about half of the mass recirculated is natural-based waste, and the other half is synthetic-based. Yet, the carbon contents are different: 47%–50%$_w$ for natural C-Materials; and 60%–80%$_w$ for synthetic materials[49]. Therefore, the carbon source is mainly synthetic C-Materials.

Table 2. Waste mix projection and its properties

Waste	Mt_{daf}	$\%_w$	H/C	VM_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}	Cl_{daf}	MtC
Wood	**102**	**19**	1.46	84.5	15.5	50.3	6.1	43.0	0.4	0.1	*<0.1*	**51**
P&C	**119**	**23**	1.60	88.0	12.0	46.7	6.2	46.6	0.2	0.2	*<0.1*	**55**
Natural TX	**27**	**5**	1.59	88.9	11.1	47.6	6.3	45.1	0.8	0.1	*<0.1*	**13**
Plastics*	**234**	**44**	1.67	96.4	3.6	79.6	11.3	4.9	0.1	0.2	3.9	**186**
Synthetic TX	**47**	**9**	0.96	89.0	11.0	59.3	5.3	27.4	7.6	0.5	0.0	**28**
TOTAL	**530**		**1.55**	**91.2**	**8.8**	**63.1**	**8.4**	**25.7**	**0.9**	**0.2**	**1.7**	**335**

**36%PE, 20%PP, 7%PS, 11%PET, 6%PVC, 6%rubber + others (carbon content for PE/PP 85-86%$_w$, 40%$_w$ for PVC and 60%$_w$ for PET)*
P&C: Paper and cardboard, TX: textiles, daf: dry ash free, VM: Volatile matter, FC: Fixed carbon.

Carbon is the primary element in C-Materials and the most-relevant factor for closing the loop and avoiding CO_2 emissions. However, mixed waste contains heteroatoms, with about 26%$_w$ being oxygen and 3%$_w$ being nitrogen, sulphur and chlorine. Oxygen is the most abundant heteroatom, and its effects on thermochemical recycling must be considered. Of the other heteroatoms, the waste contains about 5 Mt of nitrogen, which corresponds to 3% of the ammonia produced globally[5]. For sulphur, the waste has the equivalent to 1% of worldwide production[50] (≈1 MtS), and there is about 15% of the global chlorine production[51] (≈9 MtCl).

Table 2 also shows the estimated proximate analysis of the waste, indicating in which form the carbon is found. Mixed waste also has a substantial amount of Fixed Carbon (FC). About 9% of the weight is FC, which corresponds to about 16% of the carbon in the waste. As FC is usually converted by gasification or combustion, producing syngas or CO_2, it does not contribute directly to the yield of HVC. Consequently, a strategy to recover the FC when choosing the thermochemical process that converts the waste into chemicals is needed.

A preliminary observation was that certain aspects need to be considered to convert all the carbon into products, so as to close the carbon cycle. There are different sources of carbon (natural and synthetic), and the utilisation of FC is necessary. In addition, a strategy to deal with heteroatoms is needed.

Towards net-zero emissions

As previously mentioned, in the projected C-Materials system, the emissions originating from the carbon in materials will be reduced by half, and the remaining emissions will consist almost exclusively of bio-based carbon. Under the condition that biomass extraction has a neutral impact on land carbon stocks and sink strength, the proposed scenario would represent a functional deposition, or carbon sink, of 1 $GtCO_2$. This sink results from interpreting the stock as long-term carbon storage that remains in the system in the form of products (190 MtC and 90 MtC of natural and synthetic materials, respectively), as depicted in Figure 5.

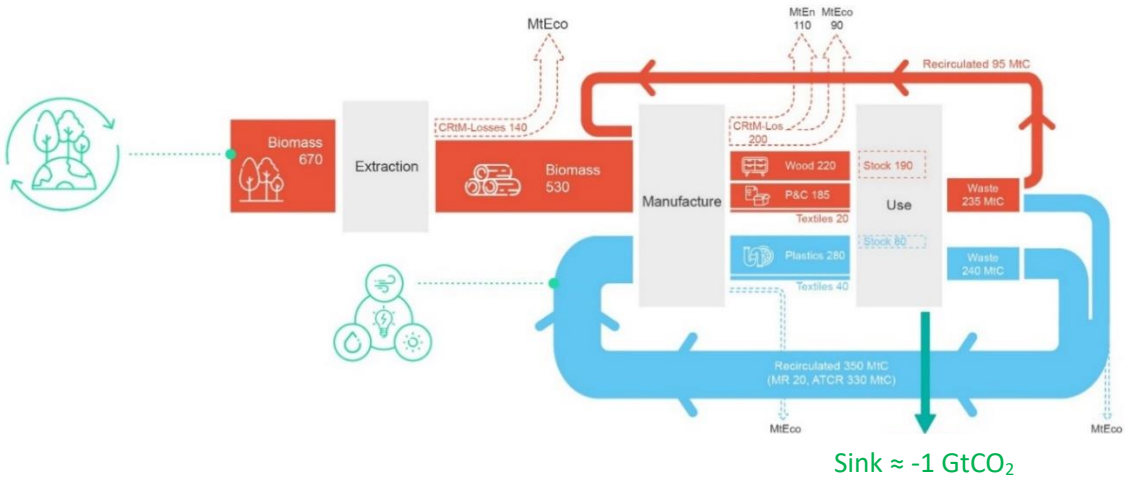


Figure 5. Potential negative emissions of the C-Materials system when using renewable energy and sustainably sourced biomass.

To achieve net-zero emissions, we need to tackle material-related emissions and energy-related discharges. The levels of these emissions depend on the energy consumption and how the energy is produced. The energy demand of thermochemical recycling is estimated to require 18±7 EJ (*Paper I*). Even though the demand is lower compared to the current system, given that the extraction of fossil carbon has an energy demand of 21±1 EJ, this is still a considerable energy need. For an average energy need of 18 EJ and a carbon intensity of 130 $kgCO_2/GJ$ (global average), the energy-related emissions from thermochemical recycling will reach 2.4 $GtCO_2$, while if a fully renewable system is considered, i.e., 2 $kgCO_2/GJ$[52] for wind energy, 0.04 $GtCO_2$ will be emitted.

While the proposed system reduces current carbon emissions by half and the amount of energy used is likely lower, it does not ensure net-zero emissions. It is evident that energy-related emissions have a prominent impact on the total emissions and depend strongly on the energy source, and that the availability of renewable and low-carbon electricity is paramount. In addition, biomass extraction must have a neutral impact on the ecosystem. Both constraints, renewable energy and sustainable biomass supply, are essential for net-zero emissions. Nonetheless, there is scope for 1 $GtCO_2$ of negative emissions with these constraints being met.

Thermochemical recycling of C-Materials

The previous section showed that the carbon in post-consumer waste is sufficient for the supply of primary chemicals used for synthetic material manufacturing. It also illustrated that the available waste has an approximate composition of 63%$_w$ carbon, 8%$_w$ hydrogen, 26%$_w$ oxygen, and 3%$_w$ other, and consists of a mix of natural and synthetic C-Materials.

The aim is to convert these C-Materials into HVCs and methanol via thermochemical recycling. However, the diversity of the waste composition makes it difficult to predict the optimal conditions for the process, as the yields are highly dependent upon the molecular structures within the waste stream. Thus, this section introduces the thermochemical conversion of various wastes from the theoretical point of view, as well as experimental results from the decomposition of a mixed waste that resembles the projected available waste.

Thermochemical conversion of carbon materials

Thermochemical conversion aims to decompose the macromolecules into smaller molecules while preserving parts of their structures. For solids, such as C-Materials, the thermal decomposition starts with drying, followed by the devolatilisation of the dry fuel. The devolatilisation or pyrolysis step involves a series of complex chemical reactions that are endothermic in nature, and leads to the generation of volatiles (gases and tars) and a solid residue. This solid, which is referred to as char, consists mainly of carbon (FC) and ash. The char formed depends on the nature of the material. In general, natural carbon materials like cellulose or lignin produce more char compared to plastics. For instance, for PE, PP and PS the FC is negligible, while for other plastics, 7%$_{daf}$, 11%$_{daf}$ and 25%$_{daf}$ for PET, PVC and PUR, correspondently. Similarly, natural C-Materials have an FC content in the range of 7%–20%$_{daf}$ for materials with high cellulose content, up to 40%$_{daf}$ for high lignin content.

Gasification process aims for maximum conversion to a gas product or syngas, including char conversion into products. This process involves several steps and complex chemical reactions, although it can be summarised by the following steps: drying, pyrolysis, reactions in the gas phase (cracking, reforming and others), and heterogeneous char gasification, as depicted in Figure 6.

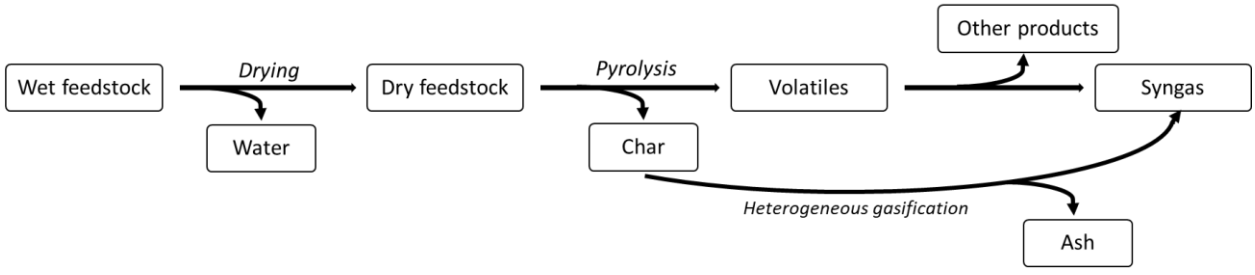


Figure 6. Thermal decomposition of solids including char gasification.

The thermal decomposition of polymers (synthetic and natural) is a complex process that is still being researched, yet some general trends have been observed experimentally. The devolatilisation or pyrolysis can be promoted by high heating rates and high process temperatures. Combining these operating conditions is usually referred to as 'process severity', whereby a higher severity corresponds to a higher temperature as well as longer residence time. The operating conditions (severity) can be optimised for each polymer to form monomer structures and other desired molecules from the plastic feed, such as aromatic compounds and base chemicals. However, too high severity leads to secondary reactions that might be undesired, forming unwanted products such as soot. Figure 7 summarises the most common polymers and its decomposition pathways found in literature[28,38–40,45,53–59].

For common polyolefins such as PE and polypropylene (PP), at low temperature, the decomposition yields wax/aliphatic oils, and the trend is towards light olefins when the temperature and process severity are increased. Polymers that contain aromatics, such as polystyrene (PS) and PET, and natural polymers, such as lignin, lead to the release of aromatics during thermal decomposition.

Other natural polymers, such as cellulosic polymers (paper, paperboard and cotton), have a high oxygen content (O/C=0.85) in the forms of hydroxyl (OH-) and C-O-C bonds between the glucose monomers. A high oxygen content usually promotes the production of shorter oxygenated hydrocarbon fractions, which further decompose to produce CO and CO_2. Oxygen-containing polymers such as polyesters also decompose. Similarly, the ester linkage eventually splits to CO_2 if there is sufficient process severity.

Several widely used polymers contain heteroatoms other than oxygen, such as sulphur, chlorine, and nitrogen. Heteroatoms may constitute highly reactive or, in other words, weak bonds in the molecule and, therefore, provide preferred thermal decomposition paths and the generation of smaller stable molecules such as H_2S, HCl, NH_3 and HCN. For example, the dehydrochlorination of PVC occurs at around 300°C, producing HCl[58]. However, if the process severity is low, the heteroatoms remain in the hydrocarbons, rendering their recovery difficult. For instance, polyurethanes (PUR) and polyamides (PA) contain nitrogen in the inter-monomer bond, while polyacrylonitriles (PAN) contain nitrogen in the form of cyanide. Aliphatic PU and PA have relatively low thermal stability, given that the amide and urethane linkages re-arrange readily at temperatures in the range of 250°–450°C. This rearrangement can lead to linear fragments that contain the functional groups -amino ($-CH_2-NH_2$) and -nitrile (-CN).

As shown in Figure 7, the products depend heavily on the process severity and molecular composition. At high process severity, the products are mainly light olefins, one-ring aromatics (BTX) and syngas, having lower-level dependency on molecular composition than at low process severity. A high-severity process is beneficial for obtaining the targeted chemicals, i.e., HVCs and methanol, and for decomposing a heterogeneous waste. In addition, at higher temperatures, heteroatoms are less likely to be present in the produced hydrocarbons.

Avoiding undesired secondary reaction at elevated temperatures generally high heating rates and short gas residence times (in the order of seconds) of the pyrolysis products are beneficial. For plastics, a high heating rate is also significant because their poor heat conductivity reduces their rate of thermal decomposition, primarily when the reactor cannot provide high heating rates[60].

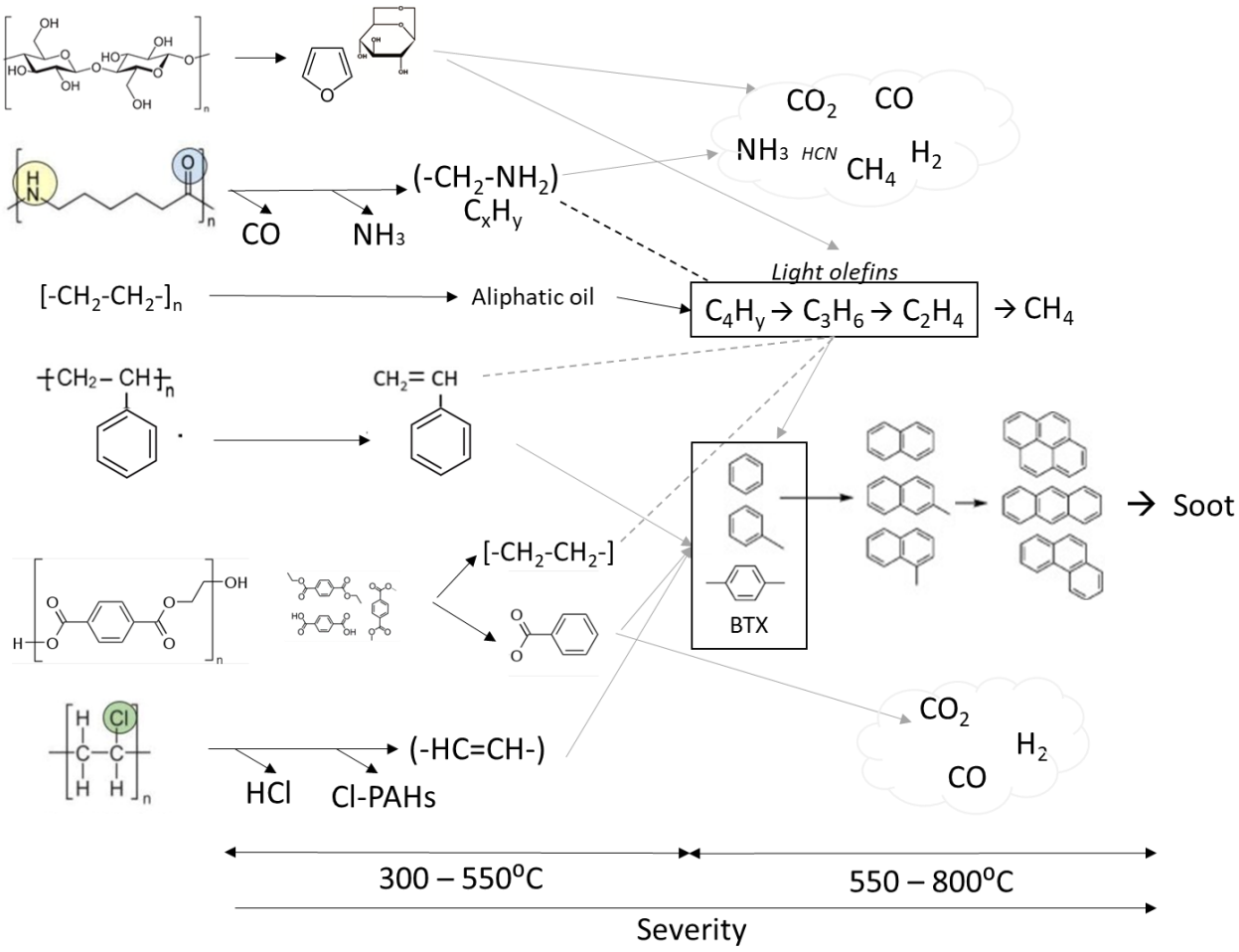


Figure 7. Schematic of polymer thermochemical conversion with process severity.

The conversion of char is an additional relevant factor for the thermochemical conversion of mixed waste. The char content of mixed waste ranges from 8%$_{daf}$ to 14%$_{daf}$, which corresponds to up to 26%C of the total carbon in the fuel. Thus, a process that recovers this carbon is crucial for achieving a circular economy. In contrast to pyrolysis, the produced char or FC is converted into gas products during gasification. If the gasification agent is steam, the fuel is decomposed into CO and H_2 at temperatures in the range of 550°–1,000°C. Both pyrolysis and gasification are endothermic, requiring energy in the form of heat. An alternative is to combust the char to produce energy, which can be used for thermal decomposition/pyrolysis. However, this produces CO_2, which can be recovered through CCU, although this requires additional energy for capturing and in form of hydrogen to synthesise products such like methanol or Fisher-Tropsch crude.

The formula shown below aims to simplify the thermal conversion of mixed waste under high severity conditions, i.e., at high heating rates and high temperatures. The term CHONSCl generically represents the mixed waste. The other terms are fixed carbon (Cfixed), hydrocarbons (C_xH_y), CO, CO_2 and H_2, and the products produced from heteroatoms, such as H_2S, HCl and NH_3. In addition, char gasification or combustion is also represented.

$$CHONSCl \rightarrow C_{fixed} + C_xH_y + CO + CO_2 + H_2 + NH_3 + H_2S + HCl$$
$$C_{fixed} + H_2O \rightarrow CO + H_2 \quad or \quad C_{fixed} + O_2 \rightarrow CO_2$$

The shares of products HC, CO-CO_2 and H_2 depend on the molecular structure of the polymer waste and the process conditions, and are not predictable; thus, it is necessary to study the product distribution of the mixed waste experimentally. In addition, although the heteroatoms are represented in the product slate as H_2S, HCl, NH_3, it is unclear as to whether there are heteroatoms remaining the hydrocarbons. To evaluate carbon recovery, it is crucial to understand and predict the potential for monomer and chemical recovery from the various polymer mixtures.

Experimental set-up

The technology employed was chosen considering that the process must handle diverse types of mixtures and be able to provide high heat transfer and high temperatures (700°–850°C). Among the different thermochemical methods already studied, the Fluidised Bed (FB) concept has proven suitability for non-homogeneous fuels, such as waste fractions that have low heat conductivity and materials with high plastic-content[42,44,61].

Three mixed wastes, containing different mixtures of C-materials, were studied. Cable plastics (CP) was studied due to their high polyolefin content and high chlorine content, to evaluate the effects of heteroatoms on the conversion process. The two other wastes were textiles (TX) and automotive shredder residue (ASR), which are highly heterogeneous. TX and ASR have similar elemental content as the available waste, and they serve as a model for understanding the products obtained from mixed waste.

Chalmers gasifier

The experiments were performed in the Chalmers Research Gasification Unit, which comprises of a 10-12 MW_{th} Circulating Fluidised Bed boiler and 2-4 MW_{th} bubbling bed gasifier. A schematic of the Chalmers Dual Fluidised Bed (DFB) gasification unit is shown in Figure 9. The DFB system comprises two connected reactors, a combustor (2) and a gasifier reactor (6), where a looped sand-like bed material with high heat transfer capability acts as the heat carrier in the process. The bed material is heated in the combustor and circulated to the fuel reactor to provide the heat required for the decomposition of the waste. The boiler is fluidised with air and fed wood chips and wood pellets, whereas the gasifier is fluidised with steam and fed mixed waste. In the present study, silica and olivine sand were used as the bed materials for heat transport between the reactors.

The process was evaluated by characterising the raw gas produced in the gasifier. For quantification, Helium is added to the gasifier together with the fluidisation steam as a trace gas. Two gas streams are extracted from the raw gas stream at the position indicated with an X (Figure 8) after being cleaned of particulate matter by passage through a high-temperature filter at 350°C. The two flows are used to: (i) determine the permanent gas composition and the aromatic hydrocarbon content; and (ii) establish a carbon balance over the gasifier.

The first stream goes to a micro gas chromatograph (µGC), which measures the concentrations of H_2, He, N_2, CO, O_2, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and H_2S. Thus, the permanent gas composition is determined. A port allows sampling of the tar for the Solid Phase Adsorption (SPA) method[62]. The heavy hydrocarbons with boiling points in the range from benzene to chrysene are quantified. The hydrocarbons falling within this range are defined as tar. The second stream is reacted at 1,700°C in a High-Temperature Reactor (HTR), cracking hydrocarbons to form only H_2, CO, CO_2, and H_2O, and the dry gas goes to a second µGC. The HTR determines the total carbon from the raw gas, as described by Israelsson et. al[56].

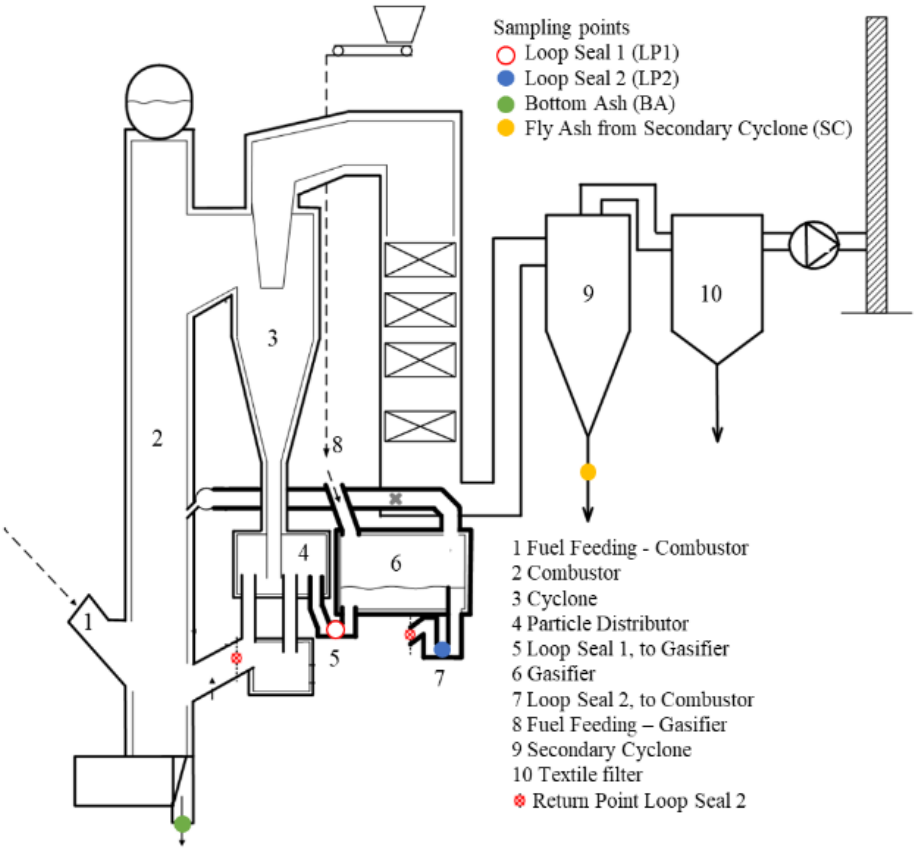


Figure 8. Schematic of the Chalmers' DFB gasifier.

The circulating fluidised bed boiler comprises the combustor (1) and the primary cyclone (3), which returns the bed to the combustor via the particle distributor (4). The bed material circulates from the particle distributor to the gasifier (6) via the first loop seal (5). The bed material returns to the combustor through a second loop seal (7), which is connected to the return leg of the combustor. The positions of the fuel feed-points to both the combustor (2) and gasifier (8) are indicated by arrows. Lastly, the raw gas is fed to the boiler.

As shown in Figure 9, the carbon in the product is distributed between four fractions: permanent gas (CO, CO_2, CH_4, C_{2-} and C_{3-}hydrocarbons), SPA tar (measured aromatics), and non-identified (aliphatic from C_3+ and unidentified aromatics), which can be determined from the total Carbon converted in the HTR. Finally, the unconverted fraction can be calculated given the carbon content in the fuel.

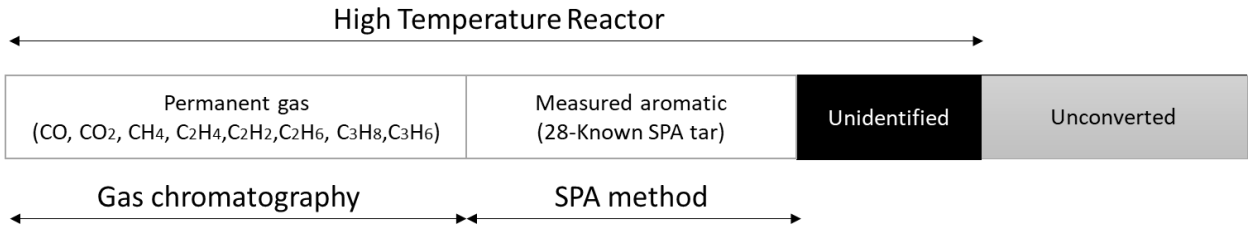


Figure 9. Distribution of the carbon in the product fractions. The measurement methods used to characterise the fraction are indicated.

For ASR and CP, the SPA method was performed using one amine for the absorption of the aromatic fraction. The analyses showed a high variation in the benzene content within samples. At the same time, the non-identified fraction was relatively high compared to experiments using biomass. Thus, additional method development was carried out by conducting lab tests to investigate how to improve the absorption. Results showed that the benzene found with double amine is 2-3 times higher than the measured with single amine. Thus, the method was improved for the TX experiments, using double amine, while for CP and ASR, the benzene was estimated to be 3 times higher than the measured.

The original SPA method quantified 28 hydrocarbons with boiling points in the range from benzene to chrysene, including BTX, styrene, biphenyl, naphthalenes, 3- and 4-ring aromatics. Among those hydrocarbons, seven are oxygen-containing compounds, i.e., phenols and furans. Given that mixed waste has a considerable amount of nitrogen, the method was improved by adding the quantification of aniline, benzonitrile and p-tolunitrile, and use for all three wastes. Additionally, GC-MS analysis of all samples was performed to estimate the unknown aromatics in the SPA, to further study the carbon distribution, as well as to investigate the heteroatoms in that fraction. The GC-MS estimated aromatics comprise compounds with carbon numbers of C_6 to C_{22} as determined by weight with an uncertainty of ±20%.

Waste and operating conditions

Three distinct mixed wastes were studied to assess the possibilities and limitations associated with thermochemical recycling. As enumerated at the beginning of this section, the three feedstocks used were: textiles waste (TX); automotive shredder residue (ASR); and cable plastics (CP). The main operational conditions are indicated in Table 3. The severity of the process was similar for all the mixed waste experiments. The temperature range was

800°±10°C and the steam-to-fuel ratio was 1.0±0.1. The main difference was the bed material. Whereas silica sand was used for TX and CP, olivine was used for ASR.

The waste residues have different characteristics in terms of their elemental composition and, thus, distinct H/C and O/C ratios (see Table 3). The carbon content is 60%$_w$ and 66%$_w$ for TX and ASR, respectively, and significantly higher, 79%$_w$, for CP. The hydrogen content is also higher for CP, 12%$_w$, and lower, 5%$_w$ and 8%$_w$ for TX and ASR, correspondingly. Similarly, the oxygen content is higher for TX and ASR, while is very low for CP.

Table 3. Operational condition and characteristics of the mixed wastes.

	Textiles (TX)	**Automotive Shredder Residue (ASR)**	**Cable Plastic (CP)**	**Estimated mixed waste**
Operational conditions				
Temperature	*800°±10°C*	*790°C*	*800°C*	*-*
Steam to fuel ratio	*1±0.05*	*0.9±0.05*	*1±0.05*	*-*
Bed material	*Silica sand*	*Olivine*	*Silica sand*	*-*
Elemental analysis %$_{daf}$				
C	*60.1*	*66.3*	*79.2*	*63.1*
H	*5.44*	*8.03*	*11.81*	*8.4*
N	*3.85*	*2.40*	*0.03*	*0.9*
S	*0.16*	*0.43*	*0.03*	*0.2*
Cl	*0.13**	*1.35***	*8.06*	*1.7*
O	*30.2*	*21.5*	*0.9*	*25.7*
Ash (%dry)	*1.3*	*39*	*28*	*--*
Ratios and proximate analysis				
H/C	*1.1*	*1.45*	*1.8*	*1.6*
O/C	*0.4*	*0.2*	*0.01*	*0.4*
VM (%C)	*81%*	*88%*	*96%*	*84%*
FC (%C)	*19%*	*12%*	*4%*	*16 %*
Polymer content estimate %$_w$				
Cl-containing polymers	*≈0.2%*	*≈2%*	*14-15% PVC*	*≈3%*
N- containing polymers	*10±1% PA (Nylon) 9±1%Acrylic*	*23±4% PUR and PA*	*≤0.2% PA*	*≈5%*
O-containing polymers	*72±1% Polyester 9±1% Cotton*	*40±8% Polyester, wood (≈10%) & others*	*-*	*≈12%PET/Polyester 28% P&C & cotton 19% wood*
Linear polymers (H/C≈2)***	*-*	*34±8% PE/PP*	*85-86% PE&PEX*	*25% PE/PP*
Others	*-*	*-*	*-*	*3%PS +5%others*

**Includes 0.008% F; **Includes 0.25% Br; ***Linear for N/O-containing polymers not included.*

The ultimate analysis was obtained via thermogravimetric analysis (TGA). VM: volatile matter and FC: fixed carbon.

Not only are there differences in the elemental compositions of the waste but also in the material that they contain. Textile waste is a heterogeneous blend of synthetic and natural C-Materials. About 70% of the TX is polyester, while other synthetic textiles, such as nylon, acrylic and elastane are found in this waste. In addition, significant amounts of cotton, wool together with artificial cellulosic fibres are present. ASR is a plastic-rich fraction that is acquired when

rejected cars go through mechanical recycling. This fraction is a highly heterogeneous stream that contains a mixture of plastics, e.g., PUR, PA, PMMA, ABS, PP, PET, PVC, PBT and PC, as well as wood and textiles with up to 50% inorganics, e.g., fillers, metals and glass. The CP waste is also a left-over fraction from cable metal recycling. Desirable metals are mechanically separated, leaving a shredded plastic fraction. Cable plastic is composed of a blend of polymers: PE, cross-linked polyethene (PEX) and polyvinylchloride (PVC).

An estimate of the polymer contents is included in Table 3. The estimation was done by fitting the total CHO content against the CHO content of the plastics present, together with other constraints, different for each waste, that are explained below:

- For CP, the estimation is based on the fact that the Cl content in PVC is 55%–57%$_w$, such that one can estimate the total PVC, while the remainder is PE and PEX. The low Nitrogen content is likely to be nylon (0.2%).
- For TX, the estimation was carried out using garment identification with an automatic sorter equipped with an infrared sensor (sorting into 21 categories, including the most common textiles and blends). Overall, 90% of the weight was characterised, with the remaining 10% being estimated from the elemental analysis.
- For ASR, the estimation is based on the elemental analysis and an understanding of the polymer content of cars 10-20 years ago, since that is the average lifetime of automotive products[33,64]. However, given the diversity of materials, there is considerable uncertainty on the contents of the polymers.

As can be seen, the polymer content of the waste was divided into Cl-, N- and O-containing polymers together with linear and others. Most of the polymers in TX waste are oxygenated, 80%$_w$, together with about 20%$_w$ of nitrogen containing plastics. ASR contains a similar share of N-containing polymers, while only about 40%$_w$ of oxygenated and about 35%$_w$ of linear polymers. On the contrary, CP mainly contain linear plastics, ≈85%$_w$, and the rest is PVC. It must be noted that some of the N- and O-polymers contain aromatic rings as well as linear polymers. CP has the highest share of linear plastics follow by ASR and TX. The opposite happens for aromatic polymers, TX is mainly composed of aromatics, followed by ASR, while the share in CP is negligible.

The polymer and elemental composition of the estimated waste (right column in Table 3) have similarities and differences compared to the studied wastes. TX and ASR have a closer CHO composition and proximate analysis to mixed waste, compared to CP. The major differences are nitrogen and chlorine content. TX and ASR have higher N-content and lower Cl-content than the mixed waste, while CP has five times more chlorine and much less oxygen. These different heteroatoms compositions help to identify its effects in the product distribution.

As previously explained, the type of polymer also plays a role in the products. The main difference between the studied waste and the estimate mixed waste is the content of cellulosic

materials. Most of the polymers in mixed waste are cellulosic (≈47%$_w$), while that not the case for the studied wastes (about 10%$_w$ for TX and ASR, and none for CP). However, it is likely some cellulosic materials to be separated streams (paper, wood), having a lower concentration in mixed wastes. When it comes to aromatic and linear polymers, TX is composed of mainly aromatics, CP of linear, and ASR is a mix of both. The latter is similar to the estimated mixed waste. Overall, having different material compositions aids to identify its effects in the product distribution.

Results: Carbon distribution

Measured carbon products

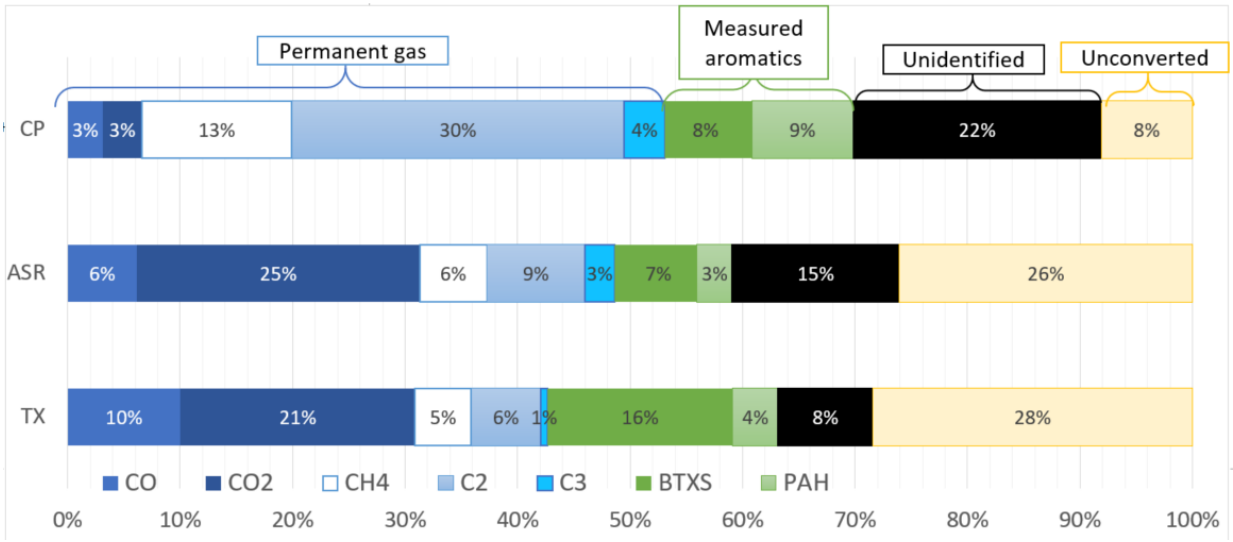
Figure 10a shows the measured carbon distributions of the products derived from the conversion of the three types of mixed waste under similar operating conditions. The products can be divided into permanent gas, aromatic fraction, unidentified, and unconverted. Most of the carbon is present in the form of permanent gas, at 43%–53%C. The measured aromatic fraction ranges 10%–20%C and the unidentified is 8%–22%C. In addition, there is a significant amount of the carbon not converted, i.e. 8%–28%C.

There is a strong correlation between the structure of the waste and the share of products. The share of permanent gas increases at higher H/C ratios. Higher content of linear hydrocarbons translates to a higher content of C_2-C_3; for CP it is 33%C, for ASR it is 11%C, and for TX it is 7%C, in descending order with descending order of linear content. For example, the gas composition of CP contains mainly CH_4 and C_2-C_3, with only a small fraction of CO-CO_2. In contrast, the gas compositions of ASR and TX contain mainly CO_2, reaching 20%–25%C in this form.

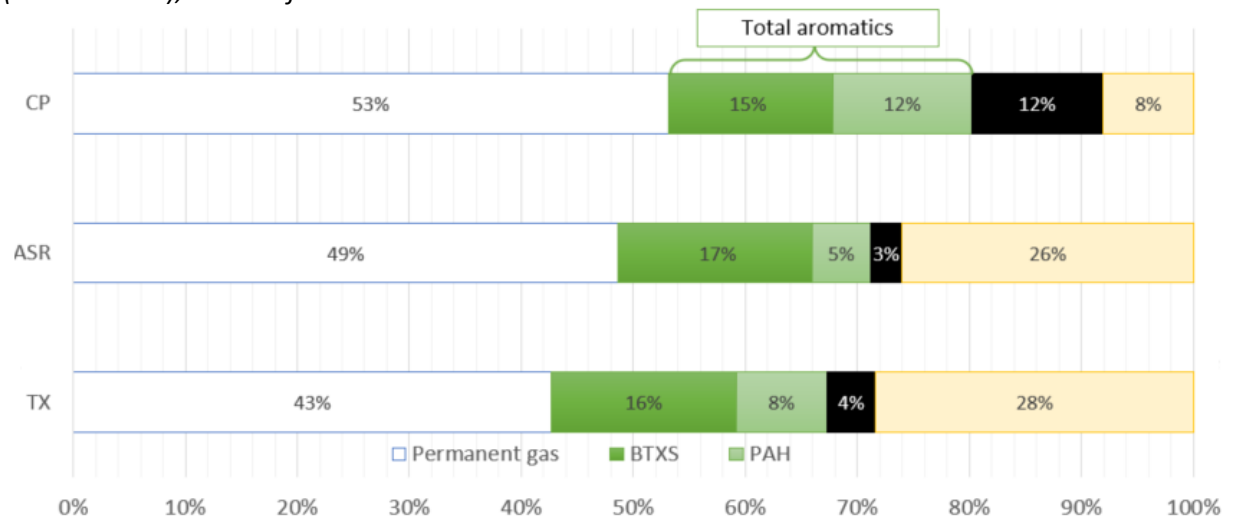
The quantity of the aromatic compounds also differs among the waste types. The aromatic compounds consist of BTX and polyaromatic hydrocarbons (PAH). The total measured carbon contents of aromatics were 17%C in CP, 11%C in ASR, 21%C in TX. Most of the aromatics were BTX, for ASR, 7%C, and TX, 16%C, while the measured PAH for CP was higher than the BTX. The highest share of PAH is for CP, 9%C, compared to 3%C and 4%C for ASR and TX, respectively. This can be explained by the decomposition of PVC, which is known to lead to high aromatization after the dehydrochlorination step.

Estimated aromatic fraction

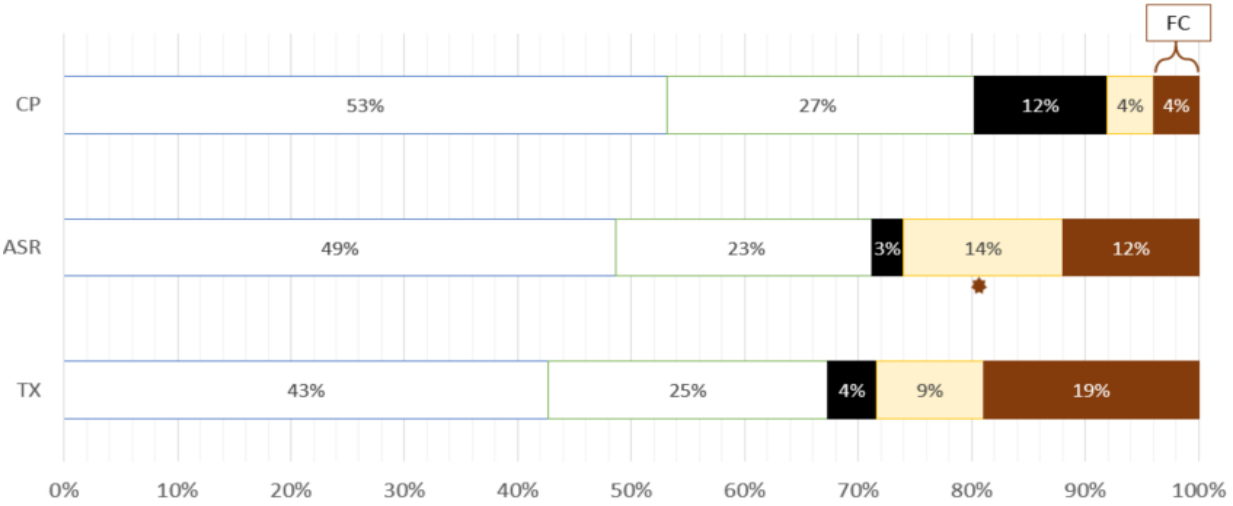
The estimated benzene and PAH are included in Fig. 10b, resulting in a total aromatic content of 27%C in CP, 23%C in ASR, 25%C in TX. As explained in the ‘Chalmers gasifier’ section, the PAH was estimated by using GC-MS analysis, resulting in an uncertainty ranging ±0.5–0.8%C in carbon basis. The benzene content of TX remains the same, given that the measurement was improved, and we assume all benzene was measured. For the others, the benzene was assumed to be 3 times higher, but can be 2-3 times bigger than measured with a single amine. To verify this assumption, both the results of HTR and single polymers gasification were studied.



(a) Measured carbon products including permanent gas (CO, CO_2, CH_4 and C_2-C_3), measured aromatics (BTX and PAH), unidentified and unconverted.



(b) Toral aromatic content including measured and estimated. Total permanent gas, unidentified and unconverted also represented.



(c) Carbon distribution including possible fixed carbon within the unconverted fraction Total permanent gas, total aromatic and unidentified also represented.

Figure 10. Carbon distribution from the gasification of mixed waste in the pilot-scale reactor. (a) Measured carbon products, (b) including estimated aromatics (c) including fixed carbon

For CP, we can compare to the gasification of virgin PE, which generates twice as much benzene than measured. Additionally, we know that PVC decomposition generates mono-aromatics, we assume here that the carbon content of benzene is closer to 3-fold higher, i.e., 27%C. For ASR, given the heterogeneous composition of ASR, we cannot be sure that this is a reasonable assumption.

The unidentified fraction can provide greater insight into this topic. For CP, this fraction has a H/C of 0.6, so it is likely that we have a highly aromatised fraction. The PAH with the highest carbon number detected by the GC-MS was $C_{20}H_{12}$. This compound has a H/C ratio of 0.55. Therefore, we can speculate that a small part of the unknown fraction comprises C_4–C_6 compounds (with H/C of 1–2), while the remainder is PAH. The unknown fractions H/C ratio is 0.5 for ASR and 0.8 for TX, also indicating the presence of PAH.

Unconverted fraction

A significant part of the products is unconverted fuel. The unconverted fraction, which was not characterised, can comprise char (fixed carbon), soot and, eventually, non-devolatilised fuel that leaves the gasifier reactor and is combusted in the combustor of the Chalmers plant. As a comparison, the result of the proximate analysis is given for the amount of char yielded from representative samples of the fuel (Figure 10c). The remaining differences between the char, the carbon from the HTR, and the carbon fed with the fuel are considerable, i.e. 4%C, 14%C and 9%C for CP, ASR and TX, correspondently. These differences may be attributable to carbon in the form of soot, differences in char formation under FB reaction conditions, non-devolatilised fuel or feeding deviations. These hypotheses have not yet been verified but will be discussed in the following text.

Soot formation depends on the residence time and the fuel. For instance, other authors have assessed the soot as having 1%C[55] during PE gasification under similar conditions. For PA and PUR, soot has been reported as having around 3%–4%C[59]. For mixed municipal solid waste, the soot has is 1%–8%C, at 805°C and gas residence time of 3 s. Similarly, for mixed polyolefin waste, the soot was 0.8%C[54], and the gas residence time was 5–6 s. CP contains mainly PE but the presence of PVC leads to PAH formation, which enhances the formation of soot. Thus, a couple of percentage points of carbon can be expected in the form of soot. Both ASR and TX have high contents of PA and PUR, which also generate more soot. In particular, TX has a high content of PAHs, so a few percentages points of carbon may be in the form of soot.

The char formation and **non-devolatilised fuel** are closely related, since char is the material that remains after the pyrolysis/devolatilisation process, as shown in Figure 6. Ideally, the char should consist of only carbon (or a very low H/C ratio) and ash, and both ash and FC are normally measured in the proximate analysis. Figure 10 shows the FC with a line. The percentages of fixed carbon obtained from the proximate analysis are 4%, 12% and 19% for CP, ASR and TX, respectively. Two observations can be made. First, we can speculate that no heterogeneous char gasification reaction occurs, since the unconverted fraction is higher than

the fixed carbon fraction. Second, there is a part of the fuel that does not undergo conversion, either because it does not undergo devolatilisation or there are feeding variations.

To study these effects further, the ASR devolatilisation time was estimated in the bench-scale reactor with single pellets (*Paper B*). After 1.5 minutes, about half of the volatiles in the ASR had been released. After more than 5 minutes, the devolatilisation was still ongoing, albeit at a low rate. Thus, complete devolatilisation of ASR takes place over several minutes, which is comparable to the residence time in the fuel reactor. The rate of conversion in the bench-scale reactor was higher than in the pilot scale, with 20% of the carbon being unconverted (see * in Figure 10), as compared to 27% of the carbon being unconverted in the pilot scale.

This 7-percentage points difference between FC and unconverted may be linked to the soot formed, different char yields from the two reactors or feeding variations. It is possible that it is soot and that the devolatilisation is also different. In the bench reactor, only one pellet was fed at a time, whereas in the pilot-scale reactor other factors could play a role. For instance, degassing the pellets may hinder mass transport and, thereby, the devolatilisation of neighbouring ASR pellets. Feeding variations can also play an important role in the conversion of the fuel.

There are different sources of feeding variations: a small variation in the feeding rate; variations in the fuel composition; fuel not reaching the reactor temperature due to being segregated together near the feeding point; or dust being carried with the gases.

The effects on the conversion of variations in the feeding rate should be minimized by the measurement length, 30 min under steady conditions. However, the variations can still affect the conversion. For instance, the feeding variation for CP is ±4 kg/h of the148 kg/h, i.e., ±3% C variation. Given that CP has an FC of 4% and the soot may account for a couple of percentage points, this leaves 2%–3% of the carbon unconverted, which is within the variation in the feeding.

Variations in the fuel composition can also lead to a defective carbon balance. Thus, the TX fraction was analysed in detail to detect possible variations in the elemental and polymer compositions and the proximate analysis. Four different batches of TX were tested in the elemental and proximate analyses, and the deviation was always smaller than 1%. The material composition was also analysed, resulting in a deviation of ±2% in the material content. Nevertheless, the thermal decomposition did not show significant differences. Thus, we conclude that fuel heterogeneity does not significantly affect the conversion.

The problem of fuel not reaching the reactor temperature can be caused by segregation in the feeding leg or dust flying away. Pellets may segregate together near the feeding point, which may cause a local temperature drop due to the heat required for devolatilisation and melting, which may be sufficient to decrease the devolatilisation rate. This phenomenon was observed

during TX feeding, whereby a significant amount of fluffy material became stuck in the feeding shaft. Dusty and/or light materials can fly away if they do not reach the temperature necessary for devolatilisation. This may have happened during the CP experiments since combustion in the raw gas line happened after the end of the experiment. However, neither of these effects was observed for ASR.

Heteroatoms influence hydrocarbon recovery

As stated above, the largest part of the heteroatoms is oxygen, and at the studied temperature of 800°C, the oxygen is mainly present as CO and CO_2 in the lighter fraction of the gas. Figure 11 shows the light fraction of the gas, which includes syngas (CO + H_2), CO_2 and methane. The syngas can be potentially used in different synthesis processes, if it has a suitable H_2/CO ratio in the range of 2–4. However, the CO_2 and methane will need to be converted into syngas to be recovered. For instance, to produce methanol, the synthesis requires a H_2/CO ratio of 2 or 3, depending on the process. Given that the total H/C ratio is around 1 for ASR and TX, there is a deficit of hydrogen to produce methanol. In contrast, for CP this gas fraction has a high H/C ratio, although this is mainly due to the high methane content, which will need to be transformed into syngas.

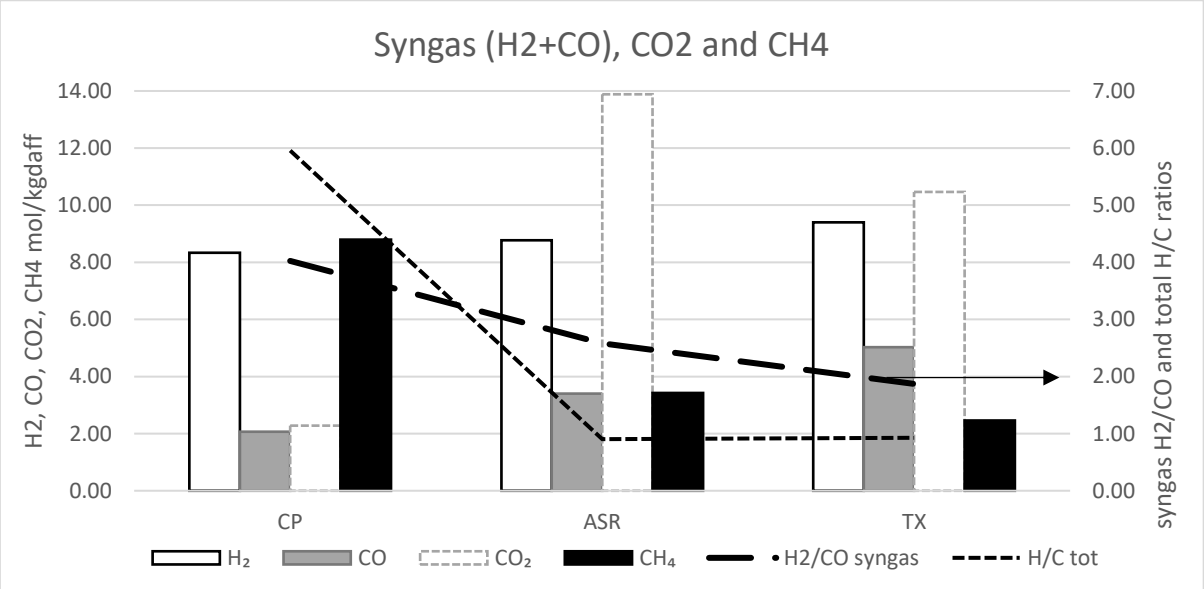


Figure 11. Bars: Syngas, CO_2 and methane gas distributions for mixed waste. Lines: syngas H_2/CO ratio and total gas H/C ratio

The presence of heteroatoms in the aromatic fraction is also relevant for its recovery. At 800°C, the oxygenated aromatic compounds were found to make up around 0.2%–1.0% of the total aromatics. Moreover, none of the aromatics is found in the boiling point range covering benzene and styrene. From *Paper B*, we know that a higher reactor temperature reduces the levels of oxygenated compounds, confirming that a higher temperature facilitates the recovery of the hydrocarbons.

The chlorinated compounds were examined in detail for ASR, starting with the GC-MS analysis at low (670°C) and high (800°C) temperatures. The results show that while some Cl-containing compounds are found at low temperatures, none are found at high temperatures. Similar results were found for CP. Further analyses were carried out to measure the dioxins in the FB reactor gas line for ASR. These measurements showed two main results: 1) that under a steam atmosphere (compared to an oxygen atmosphere), dioxin formation is much lower; and 2) that the concentrations of Cl-containing compounds are under ppm levels.

In all cases, no sulphur was found in the GC-MS analysis of the aromatic compounds at 800°C and S was found in the gas in the form of H_2S. However, N-containing aromatics were found in the TX and ASR fractions. The main compounds detected were aniline, benzonitrile and p-tolunitrile, and they comprised about 6% of the aromatics generated at 800°C. Likely, acetonitrile and acrylonitrile were also present in the permanent gas, but they were not measured. Both compounds have a boiling point similar to benzene, which may hinder the separation and recovery of benzene. Therefore, the N-containing compounds need to be studied in more detail in the future.

Often, the industrial threshold for heteroatoms content in the petrochemical industry is in the order of ppm levels[65]. While the levels of S and Cl are below this threshold, the levels of oxygenated compounds are above the threshold. Further research on the N-containing compounds needs to be conducted. Thus, alternative methods to reduce the levels of O and N, or to remove them altogether, need to be found to allow exploitation of the aromatics fraction.

Perspective carbon recovery of mixed waste

The three studied wastes help us study some trends in the polymer types and heteroatoms content. A higher linear polymer content produces higher shares of C_2-C_3, but no clear relation was found between aromatic content in the polymers with the aromatic share in the products. When it comes to heteroatoms, the chlorine content in the aromatic fraction can be avoided by increasing the temperature to 800°C. Increasing the temperature also reduces the oxygen and nitrogen content in the aromatic fraction. However, the concentration of those elements may be high (ppm level) for some processes and may affect the carbon recovery and may require further separation steps.

Overall, the results showed that mixed waste gasification can lead to the direct recovery of 20%–50% C in the forms of ethylene, propylene and BTX. To achieve 100% recovery of the carbon, we also need to recover the unconverted carbon together with the carbon in the forms of CO, CO_2, CH_4 and PAHs. Figure 12 summarises the recovery of the carbon in the mixed waste estimated into the HCVs needs in the chemical industry. As depicted, some products are the same as the HVCs, while others require further transformations steps. For instance, the permanent gas could be transformed into methanol and methanol to olefins.

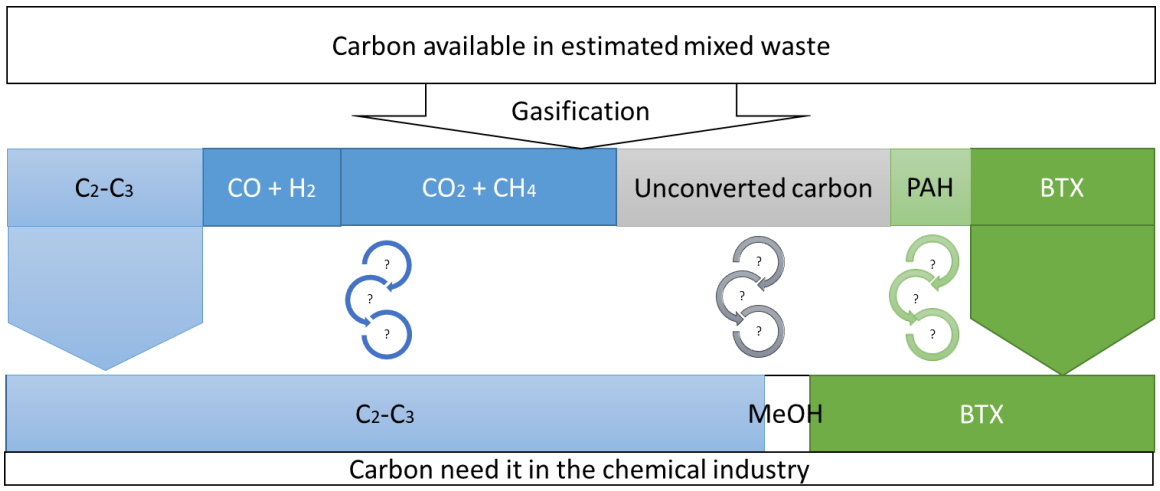


Figure 12. Carbon recovery from the mixed waste into HVCs via Gasification.

In addition, a significant share of the unconverted fraction was found, and further investigations need to be made to determine which factors contribute to this fraction. It is essential to recover that part of the carbon present in mixed waste and the PAHs. One option is to combust both the unconverted and PAHs, and use the energy produced to provide energy for the gasification process with subsequent recovery of the CO_2. However, the viability of this needs to be further studied.

Conclusions

Carbon materials such as paper, wood, plastic and textiles produce GHG emissions along its supply chain. From its extraction, manufacture and, unlike other materials, also at its end of life, releasing its embedded carbon into the ecosphere. Recycling material using current methods cannot achieve a circular economy because current recycling comes with material degradation and losses. As an alternative, this work showed that emphasizing carbon recovery, instead of material recovery, changes the perspective on carbon-containing waste flows.

The material flow analysis of the current carbon material system illustrated that the system losses are greater than the carbon material produced, and are equivalent to about 6% of the GHG. It also showed that feedstock demand for production can be covered purely by the carbon in the waste. By using this carbon, we can decouple fossil resource extraction and reduce GHG emissions by half. In addition, there is the potential to achieve negative emissions if renewable energy and sustainable biomass supply are used.

This analysis also showed that the carbon available in post-consumer waste consists of a mix of synthetic and natural C-materials, together with heteroatoms such as O, N and Cl. A potential way to recover all carbon is thermochemical recycling, which can break down materials into building blocks, similar to the chemicals employed in the petrochemical industry. As mixed waste comprises a wide variety of materials the thermal conversion of it poses a variety of challenges ranging from the unknown product distribution to the fate of heteroatoms.

The thermochemical recycling of three different mixed wastes was tested in a pilot scale reactor to understand the product distribution. The experimental results showed that the conversion yielded a mixture of gases and aromatics compounds. The carbon distribution consisted of 3%–10%C syngas, 3%–21%C CO_2, 5%–14%C methane, 7%–33%C ethylene and propylene, 15%–17%C BTX, 5%–12%C PAH and 8%–28%C unconverted. While some of these can be used directly, 33%C, if their concentrations justify separation (C_2-C_3 and BTX), the others require further recovery and processing.

Another finding is that a higher conversion temperature helps to limit heteroatoms in the hydrocarbons. For instance, the chlorine content in the aromatic fraction can be avoided by increasing the temperature to 800°C. Increasing the temperature also reduces the oxygen and nitrogen content in the aromatic fraction. However, the concentration of those elements may be high (ppm level) for some processes and may affect the carbon recovery and may require further separation steps.

Overall, the experimental investigation pointed out that thermochemical recycling has the potential to go towards a circular economy and reduce emissions. Nevertheless, further efforts are required to tackle the different challenges to make thermochemical conversion a viable recycling method for mixed wastes.

Recommendation for future work

As presented, recovering carbon from mixed waste is essential to achieving a circular economy and reducing emissions. The experimental investigation also showed areas requiring further efforts to tackle the different challenges making thermochemical conversion a viable recycling method for mixed wastes.

The results pointed out that we need to make use of syngas and HVCs (C_2-C_3 and BTX), as well as CO_2, PAH, and unconverted. While syngas and HVC can be used, further research is needed to understand how best to employ the other compounds, i.e. which transformation steps are needed to produce HCVs and methanol. In addition, it is relevant to investigate the techno-economic viability of such a process.

Further investigations are needed to elucidate mixed waste conversion, including unconverted fraction and heteroatoms. A significant part of the products was unconverted fuel, which was not characterised. This fraction can comprise char (fixed carbon), soot and, eventually, non-devolatilised fuel. Some hypotheses were posted, i.e. an estimated soot formation and fixed carbon, they have to be verified. In addition, further improvements are recommended in the sampling and analysis of samples to close the carbon balance, but also the more detailed study of the effect of heteroatoms.

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