

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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

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Abstract

Carbon-containing materials, such as paper, wood, plastic, and textiles, are essential for our daily lives, being used in everything from clothing to infrastructure. However, their use typically follows a linear pattern, in that we extract carbon resources, create products, and eventually dispose of them, thereby contributing to greenhouse gas (GHG) emissions throughout the supply chain. This linear approach has limitations, especially in terms of the recycling of these materials, with only a small fraction being recycled, often producing a lower quality product. Thermochemical recycling, which breaks down materials into building blocks, is a promising solution to close the loop of carbon materials.

An alternative perspective is to focus on carbon recovery rather than just material recovery, which could significantly change our approach to carbon-containing waste. Analysing the current carbon material system, it is clear that we lose more carbon in the system than we produce, with potential GHG emissions of around 6%. In addition, there is sufficient carbon available from post-consumer waste to produce synthetic materials, potentially reducing emissions and reducing our reliance on fossil resources. However, recycling mixed waste, which contains a variety of materials and heteroatoms, presents various challenges.

The thermochemical conversion of five different mixed wastes was tested in a semi-industrial scale reactor, to determine the product distribution. The experimental results showed that the conversion yielded a mixture of gases and aromatic compounds, with a clear correlation between the olefinic polymer content in the feedstock and the production levels of C₂–C₃ aliphatic compounds at 730°C and 800°C. The study also examined the correlations between specific bond types and product distributions, finding positive links between CO_x and C₂–C₃ and certain C–O and aliphatic bonds, respectively. Aromatics content, while not linearly correlated with the percentage of aromatic bonds, remained consistent at around 20%, regardless of the aromatics content, suggesting dependence on both aromatics content and the cyclisation of linear hydrocarbons.

Thermochemical recycling emerges as a viable method to recover carbon from mixed waste. However, challenges such as unidentified products and the fate of heteroatoms remain. Higher conversion temperatures can mitigate heteroatom levels, but further research is needed to understand nitrogenated compound distributions. While thermochemical recycling holds potential for promoting circularity and emissions reduction, additional efforts are necessary to address challenges and establish it as a viable recycling method for mixed wastes.

Further research should focus on improving sampling and analysis methods for hydrocarbons containing heteroatoms. In addition, exploring the utilization of syngas, PAHs, and other fractions, along with addressing the impact of contaminants like ash on product quality, is crucial for advancing thermochemical recycling as a sustainable waste management solution.

List of publications

This thesis is based on the following papers, which are referred to in the text according to their designated Roman numerals. The individual contributions to each manuscript are described using CRediT (Contributor Roles Taxonomy).

Publications INCLUDED in this thesis:

Paper I

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) e00124.
CRediT: Investigation, data curation, writing – review & editing (of the introduction and validation of the carbon flows).

Paper II

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. Journal of Cleaner Production 365 (2022) 132674.
CRediT: Methodology, data curation, formal analysis, validation, visualisation, writing – original draft.

Paper III

I. Cañete Vela, J. González Arias, T. Berdugo Vilches, M. Seemann, H. Thunman
Thermochemical recycling of tall oil pitch in a dual fluidized bed. Fuel 340 (2023) 127596.
CRediT: Conceptualisation, methodology, validation, formal analysis, investigation, data curation, writing – original draft, Visualization.

Paper IV

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

Paper V

I. Cañete Vela, J. González Arias, J. Maric, M. Seemann
Feedstock recycling of cable plastic residue via steam cracking on an industrial-scale fluidized bed. Fuel 355 (2024) 129518.
CRediT: Conceptualisation, formal analysis, investigation, validation, visualisation, writing – original draft.

Paper VI

R. Forero Franco, **I. Cañete Vela**, T. Berdugo Vilches, J. González Arias, J. Maric, H. Thunman, M. Seemann
Correlations between product distribution and feedstock composition in thermal cracking processes for mixed plastic waste. Fuel 341 (2023) 127660.
CRediT: Experimental investigation, data curation, validation, writing – review & editing

Publications NOT INCLUDED in this thesis:

C. Mandviwala, R. Forero Franco, I. Gogolev, J. González Arias, T. Berdugo Vilches, **I. Cañete Vela**, H. Thunman, M. Seemann

Method development and evaluation of product gas mixture from a semi-industrial scale fluidized bed steam cracker with GC-VUV. *Fuel Processing Technology* 253, January 2024

CRedit: Conceptualisation, investigation, methodology.

J. González Arias, T. Berdugo Vilches, C. Mandviwala, **I. Cañete Vela**, M. Seemann, H. Thunman

Effect of biomass ash on preventing aromatization of olefinic cracking products in dual fluidized bed systems. *Fuel* 338 (2023)

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.

Shouzhuan 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.

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. 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.

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.

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

Marie Skłodowska Curie

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List of Abbreviations

ABS: Acrylonitrile butadiene styrene
ASR: Automotive shredder residue
BTXS: Benzene, Toluene, Xylene and Styrene
C-Material: Carbon material
CBR: Cardboard recycling
CCU: Carbon capture and utilisation
CE: Circular economy
CP: Cable plastic
CRtM: Carbon resources to material
daf: dry ash-free
DFB: Dual fluidised bed
FC: Fixed carbon
GC: Gas chromatograph
GC-FID: Gas chromatograph – flame ionization detector
GC-MS: Gas chromatograph – mass spectrometer
GC-TCD: Gas chromatograph – thermal conductivity detector
GC-VUV: Gas Chromatography – Vacuum Ultraviolet Spectroscopy
GHG: Greenhouse gas
HIPS: High impact polystyrene
HTR: High-temperature reactor
HVC: High-value chemical

MFA: Material flow analysis
MtC: Million tonnes of carbon
MtEco: Material to ecosphere
MtEn: Material to energy
NIST: National Institute of Standards and Technology
PA: Polyamide
PAH: Polyaromatic hydrocarbon
PAN: Polyacrylonitrile
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
TXT: Textiles
TOP: Tall oil pitch
WEEE: Electrical and electronic equipment

Introduction

In Year 2022, the global consumption of resources was about 100 Gigatonnes (Gt), with less than 8 Gt being re-circulated back into the economic system[1,2]. These resources, which include minerals, ores, fossil fuels and biomass, are used to cover societal needs, such as housing, mobility, nutrition, and healthcare. In particular, carbon-based products, such as wood and synthetic materials, are fundamental to fulfilling those societal needs. They range from wood for furniture and construction, plastic pipes for drinking water, and synthetic materials for clothing, to the plastics used in vehicles and phones, allowing for transport and communication, respectively.

While carbon materials (C-Materials) help us to fulfil societal needs, they come with anthropogenic GHG emissions. Resources are needed to produce products, as well as to generate the energy needed to produce such products. The emissions from C-Materials have two sources: direct emissions from energy production; and embedded¹ carbon emissions from the material itself. The latter are estimated to represent two-thirds of the carbon footprints of synthetic products [3], and they are most-relevant at the end-of-life when the embedded carbon may be released as CO₂.

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. To fulfil Sustainable Development Goals, we need to provide for people's needs within the safe limits of the planet. For that, we need to both reduce resource use and limit the global temperature increase to 1.5°C [4].

Over the next 30 years, the global consumption levels 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 [5]. Thus, progression towards the circular use of materials is essential. Carbon resource consumption must be carefully considered, as it creates major environmental challenges, such as resource depletion, waste generation, and emissions that contribute to climate change.

A transition from the *take-make-waste* model to a circular one is needed to reduce carbon consumption and emissions levels. Material recycling processes are steadily increasing. However, these processes currently recycle only a small fraction of the waste and mostly single-material streams. Progression towards circularity requires processes that can treat any type of waste, including mixed waste.

Thermochemical recycling is a promising technology for converting mixed waste into feedstocks for new products. To realise the potential of thermochemical recycling, we must improve our understanding of these processes and ascertain the extent to which they can facilitate the transition to the circular use of C-Materials.

¹ Also called *Material-retained carbon*.

Aims of the thesis

The overall objective of this thesis is to increase the understanding of the thermochemical recycling of mixed waste. One aim was to gain a holistic view of how this process can be implemented. For that, a global study on carbon material flows is assessed to understand the possible flows that can be recirculated including an overview of waste available and its types. The other aim was to acquire knowledge of the steam cracking of mixed waste on a semi-industrial scale and figure out the challenges and knowledge gaps in implementing this technology.

This thesis consists of the present summarising essay and the six appended papers (**Papers I–VI**). The essay comprises the following four sections: *Background*; *Part I and Part II*, which cover the key outcomes of the appended papers; and a *Reflections* section.

The *Background* section reviews the state of the art for recycling technologies for carbon-containing materials. In addition, the different thermochemical conversion processes are discussed, including the main products generated for carbon materials (**Paper I**).

Part I describes the characteristics of the carbon material systems, and examines how to close the carbon loop using the described thermochemical recycling techniques (**Paper II**). This section describes a framework for the C-Materials flows, exploring the sizes and material contents of the flows. In addition, it explains the role of thermochemical recycling in transforming the petrochemical industry through reducing emissions, resource use and waste. Two research questions are posed to gain an understanding of how best to move from the *take-make-waste* model towards a circular and net-zero emissions economy, using material flow analysis:

- How does the global C-Materials system look today?
- Which flows and materials are available for thermochemical recycling?

Part II provides an overview of the experimental results obtained from the thermochemical recycling of mixed waste, via steam cracking, focusing on: (i) the production of valuable hydrocarbons; and (ii) the challenges encountered with mixed waste, including the measurement techniques. Selected findings from **Papers III–VI** are described. Three main questions are asked to assess the thermochemical recycling of mixed carbon waste:

- Which hydrocarbons are obtained from mixed waste processing in a semi-industrial scale reactor?
- Are there any correlations between the feedstock and product distributions?
- What measurement challenges are encountered with mixed waste?

The results are considered in detail in the *Discussions* section, together with their implications and reflections on the knowledge gaps that exist towards implementing the technology. Finally, this last section lists the conclusions of the thesis and proposes future avenues for exploration.

BACKGROUND

Recycling carbon materials

Carbon materials

Carbon materials, which are carbon-based products that are manufactured for consumer use, can be divided into synthetic materials, such as plastics and fibres, and natural materials, such as paper and wood. Carbon intersects all uses in Society. The uses of C-Materials cover numerous activity areas, including: building construction (e.g., plastic pipes and wood structures); communication and mobility (e.g., plastics in cables, phones, and cars); single-use plastics for health-care; and the many sectors that require paper and plastic for packaging purposes.

Synthetic C-Materials

Here, synthetic C-Materials are synthetic polymers, including thermoset, thermoplastics, elastomers, synthetic rubbers, and fibres². These include polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyurethane rubbers (PUR), and synthetic fibres, such as polyesters and nylons (polyamide, PA).

Despite the vast complexity of the chemical sector, most of the synthetic polymers are produced from so-called *High-Value Chemicals* (HVCs), including ethylene, propylene, and aromatics, i.e., Benzene, Toluene, Xylenes (BTX), and also some methanol. In turn, these base chemicals are produced from fossil fuel resources.

There are two main routes to obtain HVCs, from refinery by-products or via steam cracking. The steam cracker provides the majority of HVCs used to produce plastics. The feedstocks for the steam cracker are light and heavy feeds, with a split approximately in a 1:2 ratio. In addition to the cracker-sourced olefins and aromatics (accounting for about 60%), the rest are sourced directly from the refining sector [6].

The amount of HVCs needed to produce synthetic materials has been estimated at 400 Mt in 2017. However, the total level of fossil fuel resource use is unclear. According to one report[7], the chemical sector requires about 500 Mt/year of fossil fuel feedstock input to produce HVCs. It is often said that plastics use about 6% of fossil resources, although estimates range from 4% to 8%[7], which is roughly 1 Gt (given that total fossil fuel consumption is about 15 Gt per year). Another study from Year 2017 has shown that the production of HVCs requires about 500 Mt of fossil-related resources for non-energy purposes (corresponding to 25 EJ) and about 400 Mt for energy (corresponding to 20 EJ), although it is not entirely clear as to how the by-products in the refinery sector are accounted for in these estimates [6] .

Similarly, the levels of total emissions are uncertain, as they depend on the allocation of the emissions in the chemical sector and on whether the end-of-life emissions are taken into account. Carbon materials produce carbon emissions during carbon resource extraction, during the transformative production processes, and at the end-of-life (owing to incineration or

² Note that organic chemicals, such as solvents, detergents, and adhesives, are not included.

degradation in nature or in landfills). The energy- and process-related emissions from the chemical sector have been estimated at around 1.5 GtCO_{2_eq} in 2017, with about 30% (about 0.5 GtCO_{2_eq}) attributed to the production of HVCs[8]. In addition to the emissions arising from the process and energy production, C-Materials have embedded carbon emissions. These are estimated to represent two-thirds of the carbon footprints of synthetic products⁶, i.e., an additional 1 GtCO_{2_eq}.

The levels of resource consumption and emissions related to the production of synthetic materials have been increasing steadily since the 1960's, and they are projected to continue rising. In Year 2017, about 400 Mt of base chemicals (HVCs and methanol) were needed to produce about 350 Mt of plastics³. The same study projected that we will need 660–920 Mt of plastics in Year 2050, and that fulfilling this demand will require 600–1,100 Mt of HVCs and methanol.

Natural C-Materials

Here, natural C-Materials are defined as products that are manufactured from biomass resources and retain properties of the raw material⁴. They include sawn wood, wood-based panels, pulp, paper and cellulosic fibres.

The production of natural C-Materials starts with the harvesting and extraction of biomass resources by the forestry and logging industry. Harvested wood is sent to a saw-mill or the pulp industry. Wood manufacturing is the process of turning raw wood into a variety of finished products, such as wood panels. This is done using a variety of technologies, including sawing, planning, drilling, and routing. While these processes maintain most of the material properties, the pulp and paper industry separates the cellulose to produce printing paper, paperboard for packaging and sanitary paper products. There are three processes: mechanical, chemical, and recycled pulp. Mechanical pulp mostly produces packaging. Chemical pulp can provide high-quality products such as printing paper, sanitary products and packaging. Recycled pulp can only produce lower quality paper, which is used mostly for packaging purposes.

In similarity to the synthetic C-Materials, resource consumption and emissions for natural C-Materials are unclear, with projections that paper production will double by Year 2050. While statistics reveal the levels of global biomass usage and paper and pulp flows for each year[9,10], , it is unclear what shares can be directly linked to energy use and material production. Some attempts have been made to clarify these issues. For instance, Van Ewijk and colleagues have shown that in Year 2012, the total paper and paperboard production was about 400 Mt, using about 410 Mt of virgin material. In terms of emissions, another study has shown that for the same year and flows, the emissions from pulp and paper were about 800

³ Note that this reference only includes thermoplastics and thermosets (omitting fibres and elastomers).

⁴ Not that it does not include plastic such as PE made from biomass, since the chemical structure is altered.

MtCO₂_eq, i.e., about 2 kgCO₂_eq per kg of product [11]. In that study, they considered the extraction of biomass to be carbon-neutral.

It is sometimes stated that biomass resources are renewable and climate-neutral, meaning that biomass takes up CO₂ and offsets the emissions from its incineration [3,12]. However, the carbon neutrality of biomass depends on the forest/land management practices, the type of biomass feedstocks, and the time-frame being analysed [13,14]. For example, cropland expansion may cause deforestation, with consequent GHG emissions and negative impacts on biodiversity[15], as well as creating competition for food, water and land uses. Biomass is also considered to be 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[16]. Thus, there is a need for sustainable treatment of C-Materials.

While is unclear as to what levels of resources and emissions are related to C-Materials, the amounts are significant and will continue to grow in the coming years. The concept of the circular economy is a way to tackle the unsustainable use of C-Materials. The waste from C-Materials can be re-circulated to produce new materials, thereby avoiding embedded carbon emissions at the end of life and reducing resource use [2,3,17–19]. To start to understand how to close the loop, we need to have a closer look at the current recycling options and their limitations.

Recycling

To adopt circularity, we can have different strategies, change the way we use things (longer, with maintenance, reuse or/and refurbishment), the design, the collection, etc. However, ultimately, we need to recycle the materials. Currently, recycling is focused mainly on material recycling – producing a material that is the same as the original. Common examples of successful recycling today are the recycling of PET bottles to produce PET bottles once again (or polyester, i.e., PET fibres, when it does not meet quality requirements), and paper recycling into paperboard packaging. However, many limitations exist when it comes to material recycling. Thus, we need to have a clear idea of the recycling possibilities, as well as the associated limitations.

Synthetic C-Materials recycling

The recycling of synthetic C-Materials can be divided into mechanical recycling and chemical recycling. In addition, energy recovery is sometimes included in waste treatments. Each method is associated with different benefits, which make it particularly beneficial for specific locations, applications or requirements, as well as drawbacks. For instance, mechanical and chemical recycling produces recycled plastics or chemical compounds that can be used again to make new products, and energy recovery generates electricity and heat. In these methods, a portion of the resources is recovered.

Most of the plastic waste recycling that occurs today involves mechanical recycling, which consists of melting and reforming plastics into other products. This re-melting can only be done with thermoplastics and single-stream materials, such as PE, and can only produce items of the same material, which are often of lower quality due to polymer degradation. Mechanical recycling requires that the plastic waste is sorted by colour and polymer type before processing. These physical transformations are essential to produce a clean and homogeneous product for mechanical recycling. However, this process is complicated and costly. Errors can lead to materials with inconsistent properties, often rendering them unappealing to industry [20].

Polyethylene terephthalate (PET) packaging, as found in bottles and food containers, is often mechanically recycled. In Europe, about 60% of the PET bottles and containers sold on the market comprise collected waste. The recycled PET pellets can be used to produce bottles. However, when using mechanical recycling, only 50%wt of a PET bottle becomes a new bottle, although this percentage can be higher for other applications, such as trays [21,22]. Thus, only a small fraction of PET is manufactured back into products of similar quality.

PE is sometimes recycled via mechanical processes. However, the quality of the recycled material is often low. During the sorting and separation of plastics, PE/PP are often found mixed, as that have similar densities and molecular structures. Despite their similar molecular structures, they are not miscible, so the re-melting of these blends turns into a product of lower quality than the original, and it is mostly used in low-quality products such as outdoor furniture and flooring [23].

An alternative to mechanical recycling is chemical recycling. Two commonly used methods are solvolysis and depolymerisation. These consist of the recovery of the polymer and mostly focus on single-stream materials, such as sorted plastics, such as PET, PMMA and some PAs. For instance, PET solvolysis is the most-abundant recycling technique by volume. Since PET bottles are made from equivalent grades of plastics, they are suitable for the bottle manufacturing process [24]. Nevertheless, this process requires high-purity material that is free of dyes or other contaminants. For this reason, approximately 80% of the PET bottles are re-processed to polyester fibres [20,24].

Another chemical process that is being adopted more frequently is pyrolysis, which consists of breaking down the molecules into smaller pieces. Pyrolysis is often referred to as the process of producing oils that can be used as alternatives to oil-based fuels, such as naphtha. There is a strong focus on using plastic waste-derived pyrolysis oils as feedstocks for steam crackers in the petrochemical industry. However, the levels of contaminants in the pyrolysis oils of mixed waste very often surpass the technical thresholds for industrial crackers, creating costly setbacks [25]. In addition, the waste is required to have a purity level >90%, and the availability of clean feedstock is a constraint.

Natural C-Materials recycling

As mentioned above, recycled pulp can only produce lower-quality paper. In addition, recycled pulp can yield only about 80% of the input [11]. This down-grading is known as the *cascade effect*. For instance, high-quality paper fibre can be cascaded through several product life-cycles, to produce newsprint and packaging, before finally being used for energy recovery or land-filling. Recycled paper pulp is more commonly used to produce newsprint and packaging. These products usually require lower grades of paper and every time they are recycled, the fibre quality is degraded. Ultimately, the fibre becomes un-usable for material purposes[26].

In the case of timber, it is possible to convert wood to a secondary use within particleboard. Thereafter, the particleboard can be recycled one or more times into new generations of particleboard [27], eventually 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 [28].

Limitations

It is clear that C-material recycling is accompanied by down-grading, and that the techniques used only partially close the loop. Many processes do not replace the materials on a one-to-one basis, still requiring virgin resources, and they also have quality constraints. In addition, some processes, such as pyrolysis and mechanical recycling of PE/PP, target the same material streams.

While the importance of a circular economy for achieving net-zero emissions is currently a topic of vigorous debate [3,12,20,29–32], the challenges related to recycling are sometimes neglected[20]. 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 the collection, sorting, and re-processing capacity[20,33–35], and is further limited by the degradation of the material during the use phase and manufacturing process.

Most recycled materials are of lower quality than the original product[33], as depicted in Figure 1. Similarly, mechanical recycling of plastics is associated with material down-grading. For example, polyethylene (PE) packaging is recycled for moulding applications that generate lower-quality products [36].

When the plastic waste is a mix of various materials, it is necessary to separate, wash, and prepare it before recycling [37]. These physical transformations are essential to producing a clean and homogeneous product that can be mechanically recycled. Even when treated, not all of 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 contain both synthetic polymers and natural C-Materials. For both

products, the functionality, as a barrier to or enforcement of extended durability, dictates the choice of material, rather than the end-of-life considerations [33,38].

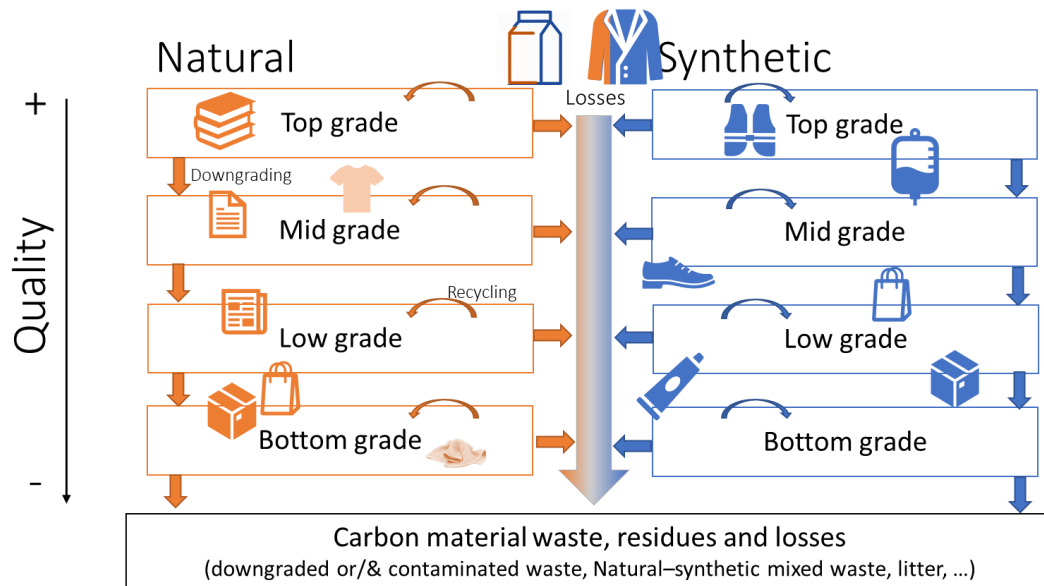


Figure 1. Cascade effect of the recycling of natural and synthetic C-Materials.

Given the current limitations of material recycling, C-Materials mostly follow a linear scheme. Wood products are scarcely recycled [27,39], and <5% of plastic waste becomes a new product [34,37,40–42]. Paper products are the most frequently recycled C-Materials, about 40% of new paper products come from recycled manufacturing [11,26]. The C-Materials that are most-commonly recycled today are single-stream flows, such as paper/paperboard, polyolefins, and PET [26,27,37].

While the current processes can recycle single-stream plastics, it remains challenging to recycle mechanically contaminated plastics. 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 efforts 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 of circularity if the fossil-derived carbon is emitted as CO₂ without further recovery [35]. Progress towards circularly using C-Materials requires a technology that can treat any type of waste (sorted or unsorted). This can be achieved by thermochemical recycling, which entails theoretically unlimited recycling of C-material, where the focus is on recovering the chemical building blocks of the materials.

Feedstock recycling

Feedstock recycling, also known as chemical recycling, thermochemical recycling or tertiary recycling, aims to convert waste polymers into original monomers or other valuable chemicals. These products are useful as feedstocks for a variety of down-stream industrial processes.

Multiple names and definitions are used; the pyrolysis process is often referred to as the thermochemical process that produces oil and gasification for syngas production. Nevertheless, pyrolysis is sometimes also used to describe the thermochemical process that directly recovers the monomers from synthetic C-Materials.

To avoid confusion, in this work, this group of feedstock recycling processes is referred to as *thermochemical recycling* and uses the same definition as in **Paper I**. Thermochemical recycling has three possible routes, as depicted in Figure 2, with an increasing thermodynamic penalty for Routes A, B and C, respectively.

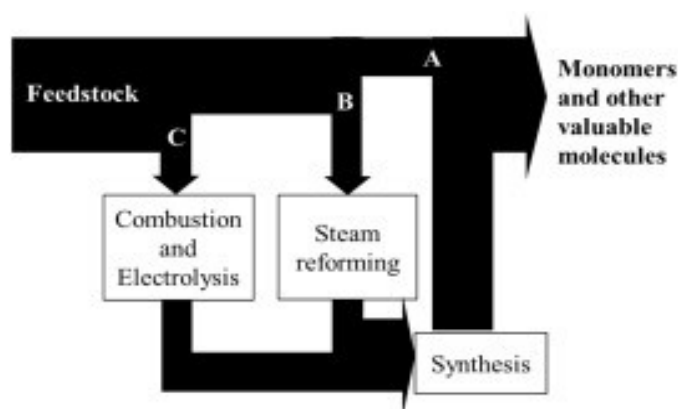


Figure 2. Feedstock recycling via three thermochemical processes.

Route A is based on the direct recovery of monomers and valuable molecules from the original material through thermal cracking of the feedstock. This route corresponds to the traditional naphtha/alkane cracking process that is currently used for monomer production, mostly olefins.

Route B refers to the thermal decomposition of the material into syngas, followed by a synthesis process. This route involves steam reforming of the hydrocarbons to CO and H₂, with adjustment of the H₂/CO ratio to suit the subsequent synthesis process. The synthesis can be, for instance, via methanol if the final product is olefins.

Route C refers to the combustion of the feedstock to cover part of the heat demand and to recover the carbon in the form of CO₂. This CO₂ stream is then used as a carbon source for the synthesis, which requires balancing of the H₂ content of the syngas (which can be produced via water electrolysis, among other processes).

Route A is preferable from the thermodynamic point of view, as it preserves the structures of the existing molecules. However, the direct formation of valuable monomers is dependent

upon the nature and composition of the feedstock applied. During thermal decomposition, part of the feedstock is inevitably converted into by-products that are not usable in the direct synthesis of plastics and other synthetic C-Materials.

Table 1 summarises the product distribution of the thermal decomposition for the most common synthetic C-materials and biomass, to give an overview of the difference of formation of valuable chemicals concerning the feedstock used.

Table 1. Summary of products of thermochemical recycling processes according to feedstock type and conditions.

Feedstock	Process characteristics	Products (%wt) [43–46]
PE	510°C pyrolysis 760°C pyrolysis 700°C pyrolysis [47] 700°C steam [47]	Gas 2%, oil/wax 98% Gas 56%, oil/wax 42% (2%char) → Monomer Ethylene 19%w + (H ₂ , CO, CH ₄ , olefins and aromatics BTX 30%) Gas 57%, oil 38% (ethylene 23%, 3% propylene, BTX 24%) Gas 76%, oil 20% (Ethylene 31%w, 15% propylene, 13% BTX)
PP	510°C pyrolysis 760°C pyrolysis	Gas 6%, oil/wax 94% Gas 51%, oil/wax 2%, aromatics 45% → Monomer propylene 4%, ethylene 14% + BTX 25%
PVC	520°C pyrolysis [48]	58%HCl, 32% oil, 8% solids
PET	Hydrolysis at 550°C	Gas 18%, solid 75% → monomer: TA 51%wt (recovery of 90% TA) for pure PET
PS	520°C pyrolysis	99% oil → Monomers: Styrene 77%
PA66 (nylon)	510°C pyrolysis 630°C pyrolysis 810°C pyrolysis 810°C steam	Gas 4%, oil 89%w Gas 30%, oil 36%w, aromatics 16% Gas 52%, oil 25%w, aromatics 23% Gas 52%, oil 26%w, aromatics 22%
PMMA	450°C pyrolysis [49]	Monomer: MMA 97%wt for pure product, 58-91% for waste, depending on ash content
PUR	750°C pyrolysis	65% gas, 7% aromatics, 13% oil, 4% nitriles, 2% HCN
Biomass /cellulose	LT 500°C pyrolysis [50] HT 810°C steam	7% gas, 85% bio-oil, 9% char for cellulose, 4%, 44% and 30%char for lignin 93% gas (syngas: 42% CO, 33% CO ₂ , 3%H ₂ , 9% CH ₄ and 6% olefins), 3% aromatics, 4% char

As can be seen, only a few C-Materials produce mainly their monomers such as PET, PS and PMMA (strictly following Route A). The thermal decomposition of PET yields about 50%wt of Terephthalate acid (TA) at 550°C, meaning that about 90% of the monomer is recovered. Similarly, PS decomposition at 520°C produces 77%wt of styrene. The thermochemical recycling of PMMA can achieve even higher recovery rates, with 97%wt of its products being its monomer MMA. This is when recycling pure PMMA, but only 58% to 91% when using plastic wastes.

In the end, Routes A and B are inter-linked, since the thermal cracking of waste often produces not only the monomers, but also other products. For instance, PE decomposition in a nitrogen atmosphere produces mostly (98%) an oil/wax product at around 500°C, while at 760°C, the oil fraction is reduced to about 40%, and the gases to about 56%. The monomer yield for the thermal decomposition of PE at 700°–750°C is only about 20%wt. In other words, 80%wt is by-products. Some of these are valuable chemicals, such as the 20–30%wt of BTX, ca. 3%wt propylene, and aliphatic hydrocarbons, but also other gases such as hydrogen, CO, CO₂ and methane, which require further synthesis. The yield of ethylene can be improved by adding steam during the thermal decomposition process. By doing so, the yield can increase to >30%wt ethylene.

Similarly, the yield of propylene from waste decomposition increases to 15%wt when adding steam at 700°C, with 13%wt BTX being formed. For PP, the thermal decomposition is similar, yielding oil at low temperatures and some monomers at higher temperature (760°C), albeit mostly ethylene (14%) and not so much propylene (4%). Still, in both cases, a significant fraction of the products is made up of by-products rather than the main monomer.

Other C-Materials, such as PVC, PA, and rubber, also yield a wide range of products and not the monomer. At low temperatures, complex oils are produced, which are problematic to use in industry due to contamination with heteroatoms. For example, PVC decomposition produces about 60%wt HCl and only about 30%wt oil, which often contains impurities (such as Cl). A similar phenomenon occurs when nitrogen is present in the feedstock. For nylon, at temperatures around 600°C, the nitrogen remains in the oil, but after HCN is released, reaching 9%wt at 800°C; in addition, significant amounts of nitriles are formed.

At high temperatures in the presence of steam, a simpler gas is produced that can be synthesised, as seen for PE/PP. Another example is biomass. Biomass gasification produces mostly a gas that consists of 42% CO, 33% CO₂, 3% H₂, 9% CH₄ and 6% olefins. This can be used to produce valuable chemicals.

As seen, during thermal decomposition not only an oil, a monomer or a syngas is produced, but a mixture of all three. The types of products obtained from thermal decomposition are highly dependent upon the feedstock and the temperature used. Thermal decomposition performed in a lower range of temperatures, 400°–700°C, produces mostly oils that can be used as alternatives to oil-based fuels, such as naphtha. Since many synthetic C-Materials are manufactured using olefins, such as ethylene and propylene, there is a strong focus on using polyolefin plastics (PE, PP) to produce pyrolysis oils as feedstocks for steam crackers in the petrochemical industry. In contrast, data relevant to the thermal cracking of mixed polymeric waste with a low content of polyolefins and a high content of other C-Materials are scarce.

Increasing the temperature, to 700°–850°C (increasing the severity), and the addition of steam promote the break-down of the molecules into smaller compounds, allowing steam cracking to

handle more-heterogeneous plastic wastes. Based on the distribution of products, steam cracking of plastic waste can substitute for existing crackers. For instance, traditional naphtha cracking produces about 25%wt ethylene, 15%wt propylene and 20%wt of other linear hydrocarbons, while PE steam cracking at 700°C produces about 30%wt ethylene and 15%wt propylene.

Steam cracking has the potential to treat mixed wastes and to promote progress towards a circular economy and reduced emissions. However, the body of knowledge on mixed waste steam cracking, as well as on its possible role in the transformation of the petrochemical industry and on a global scale, is currently incomplete.

Thermochemical conversion of carbon materials

We have seen that thermochemical recycling yields a variety of products depending on the temperature and feedstock employed. However, to gauge the potentials of these processes in terms of progress towards a circular economy, we first need to understand the mechanism behind thermochemical recycling.

The goal of thermochemical conversion is to decompose macro-molecules into smaller molecules, while preserving parts of their structures. For solids, such as C-Materials, thermal decomposition starts with drying, followed by devolatilisation of the dry fuel (*Figure 3*). The devolatilisation or pyrolysis step involves a series of complex chemical reactions that are endothermic in nature and lead to the generation of volatiles (gases and tars) and a solid residue. This solid, which is referred to as char, consists mainly of carbon (Fixed Carbon, FC) and ash.

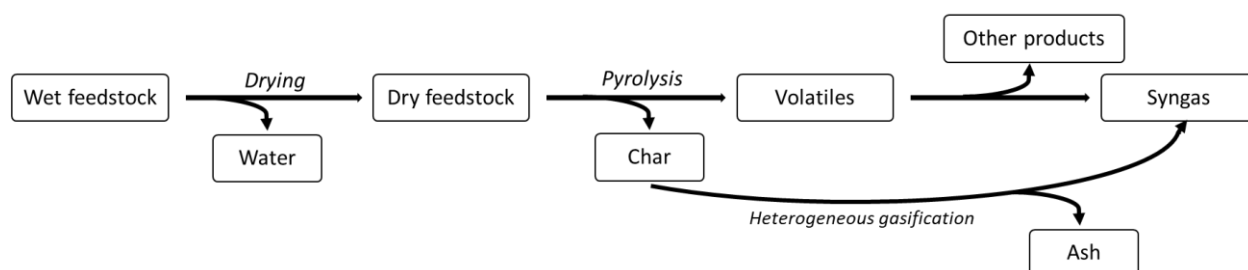


Figure 3. Thermal decomposition of solids including char gasification.

The specific char that is formed depends on the nature of the material. In general, natural C-Materials produce more FC than synthetic C-Materials. For instance, for PE, PP and PS, the amount of FC is negligible, whereas FC is about 7% for PET. For natural C-Materials, the FC is in the range of 7%–20%. As depicted in *Figure 3*, char can be converted into syngas via the heterogeneous gasification reaction⁵ in the presence of steam. In contrast, if sufficient oxygen is available, both the volatiles and char will be combusted, oxidizing further towards CO₂.

While the thermal decomposition of polymers (synthetic and natural) is a complex process that is still being researched, some general trends have been observed experimentally.

⁵ Not to be confused with the gasification process.

Devolatilisation or pyrolysis⁶ is the chemical decomposition of materials through the application of heat. This decomposition 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 a longer residence time. The operating conditions (severity) can be optimised for each polymer to form monomer structures and other desired molecules, such as aromatic compounds and base chemicals, from the plastics feedstock. However, too high a severity leads to secondary reactions that might be undesired, forming unwanted products such as soot.

For common polyolefins such as PE and PP, at low temperatures (>400°C), the decomposition consists of random scission of the polymer and yields wax/aliphatic oils, resulting in molecules of different lengths. The trend is towards light olefins when the temperature and process severity are increased to 700°–800°C, where the polymer chain breaks at the edges (end-chain scission), and secondary reactions initiate the generation of aromatic and polyaromatic compounds.

Polymers that contain aromatic compounds, such as PS and PET, and natural polymers, such as lignin, lead to the direct release of aromatics during thermal decomposition. For instance, more than 75%w of styrene is produced from PS at 510°C.

Other natural polymers, such as cellulosic polymers (paper, paperboard and cotton), have a high oxygen content (O/C ratio of 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 decompose further to CO and CO₂. Oxygen-containing polymers such as polyesters also decompose. Similarly, the ester linkage eventually splits to CO₂ if there is sufficient process severity.

Several widely used polymers contain heteroatoms other than oxygen, such as sulphur, chlorine, and nitrogen. Heteroatoms constitute highly reactive, in other words, weak bonds in the molecule and, therefore, promote preferred thermal decomposition pathways and the generation of smaller, stable molecules, such as H₂S, HCl, NH₃ and HCN. For example, the dehydrochlorination of PVC occurs at around 300°C, producing HCl [51]. 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 stabilities, given that the urethane and amide linkages, respectively, re-arrange readily at temperatures in the range of 250°–450°C. This re-

⁶ Not to be confused with the pyrolysis process.

arrangement can lead to linear fragments that contain the -amino ($-\text{CH}_2\text{-NH}_2$) and -nitrile ($-\text{CN}$) functional groups.

Figure 4 summarises the most commonly used polymers and their decomposition pathways, as found in the literature[24,47,49,51–59]. As shown, the forms of 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. A high-severity process is beneficial for obtaining the targeted chemicals, i.e., HVCs and methanol, and for decomposing heterogeneous wastes. In addition, at higher temperatures, heteroatoms are less likely to be present in the produced hydrocarbons.

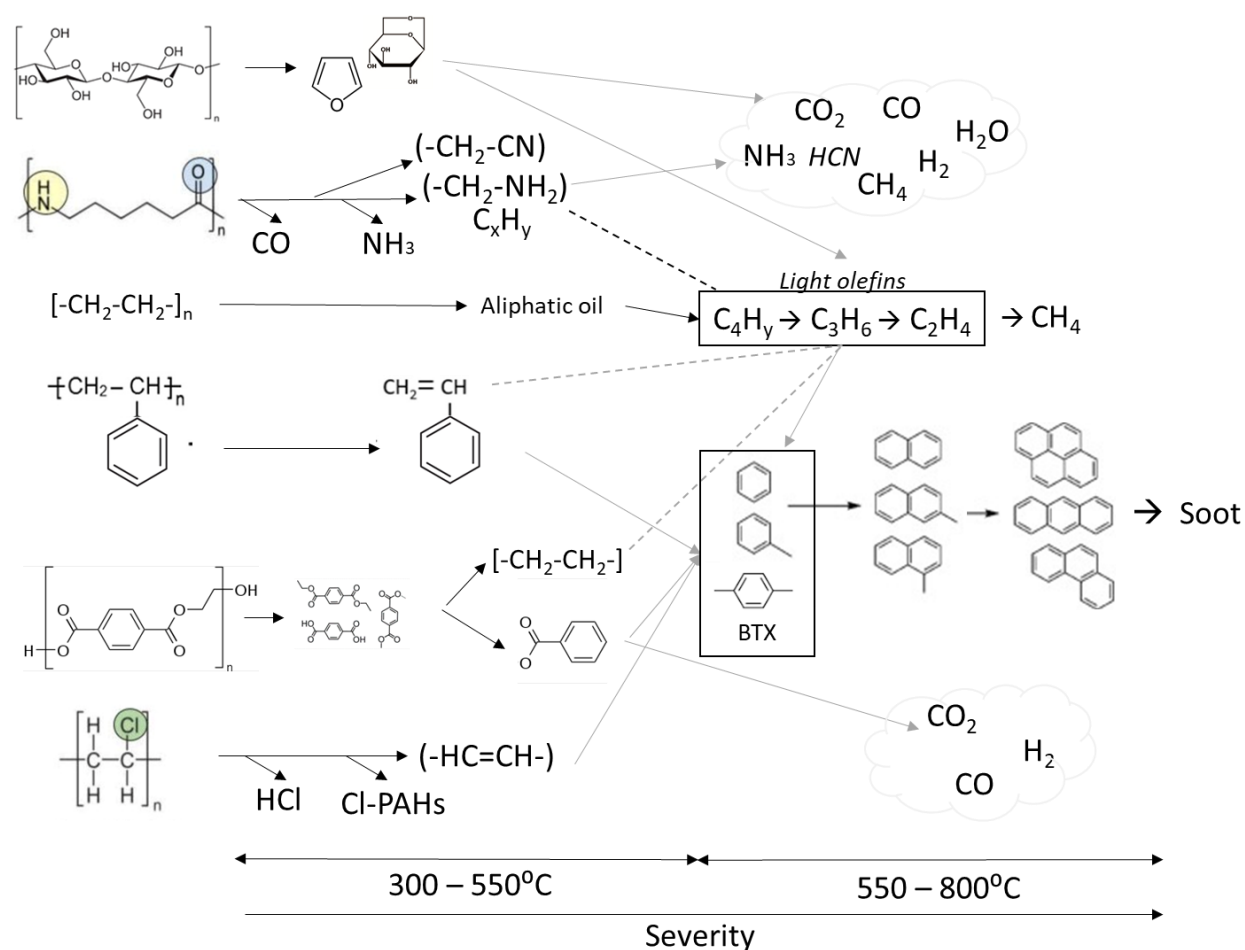


Figure 4. Schematic of polymer thermochemical conversion in relation to process severity.

Different wastes, different products, but what happens when they are mixed?

As seen in the section on recycling, waste may comprise a mixture of materials. Since the shares of the HC, CO-CO₂ and H₂ products depend on the molecular structure of the polymer waste and the process conditions. It is necessary to explore experimentally the product distribution of the mixed waste. In addition, although the **heteroatoms** are represented in the product slate as H₂S, HCl, and NH₃, it is unclear as to whether heteroatoms remain in the hydrocarbons.

To evaluate carbon recovery, it is crucial to understand the waste that is available and to predict the potentials for monomer and chemical recovery from the various polymer mixtures. Ideally, the use of natural resources should be minimised. Likewise, the demand for carbon products should be covered to the greatest extent possible by retaining all the carbon in a circular loop, such that is re-circulated indefinitely, with minimum losses to the environment in the forms of emissions and material waste.

PART I

The circularity of carbon materials

Extraction, production and waste generation

As already mentioned, the production and use of Carbon Materials (C-Materials), such as plastics and paper, entail significant waste generation, resource use and carbon emissions. The C-Materials emissions arise from energy generation and the embedded carbon in the products, both end-of-life and process emissions. The energy system can be decarbonised using renewable energy sources, such as wind or solar power. However, the amount of carbon required for a product will remain.

To understand how much carbon is required for C-Materials, a global material flow analysis (MFA) was performed for Year 2018. The details of the method used can be found in **Paper II**. The results are summarised below in terms of weight (rounded to the closest tens):

- About 920 Mt of natural C-Materials were produced in Year 2018, covering sawn wood, panels, paper, cardboard and textiles (cotton and other cellulosic fibres).
- About 430 Mt of synthetic C-Materials were produced in Year 2018, including plastics, rubbers and synthetic fibres.
- The production of C-Materials required about 1,330 Mt of biomass and 490 Mt of fossil fuel resources, excluding the resources needed for energy generation.
- The amounts of waste generated were about 520 Mt of natural C-Materials and 320 Mt of synthetic C-Materials, in other words, $\approx 55\%$ wt and $\approx 75\%$ wt of the products, respectively, were wasted in the same year.
- In Year 2018, about 210 Mt of natural C-Materials and less than 30 Mt of synthetic C-Materials were re-circulated to produce new C-Materials, resulting in less than 20%wt of the produced C-Materials being made from recycled materials.

The first observation that can be made is that, even if all the waste, about 830 Mt, is used to produce new materials, this amount does not cover the 1,340 Mt of C-Materials produced (only covers 60%wt). In addition, current recycling techniques can only recover 60–80%wt of the material weight. Thus, less than 50%wt of the products could be made from waste. All of this is assuming that those technologies can recycle any type of waste.

Employing only the current recycling techniques ensures a linear pathway, which means that the high levels of resource consumption, residue generation, and emissions persist. A serious challenge with C-Materials is their intrinsic carbon, which when lost can easily end up as carbon emissions. So, can we find a solution if we shift the focus from materials flows to carbon flows? Can this new approach guide us towards achieving a circular economy?

Carbon perspective

To answer that question, we need to know how much carbon is in the C-Material system. Here, this system includes the 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 shown in Figure 5 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.

The carbon MFA comprises three processes: *Extraction*, *Manufacturing*, and *Use*. It includes the resources and process losses for manufacturing these products, while excluding the resources needed for energy.

Extraction refers to the mining of fossil resources or the harvesting of biomass for materials 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), which are light olefins and aromatics and are the main building blocks for synthetic C-Materials.

The **Manufacturing** process involves all the transformation steps from extracted materials to products. During these processes, there is generation of by-products and waste, which are not used for materials 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 manufacturing process can also assimilate unused C-Materials from the *Use* process, such as plastic or paperboard wastes to produce new products, i.e., recycling.

The **Use** process consists of the use and end-of-life phases, 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 re-circulated back to the industry for recycling.

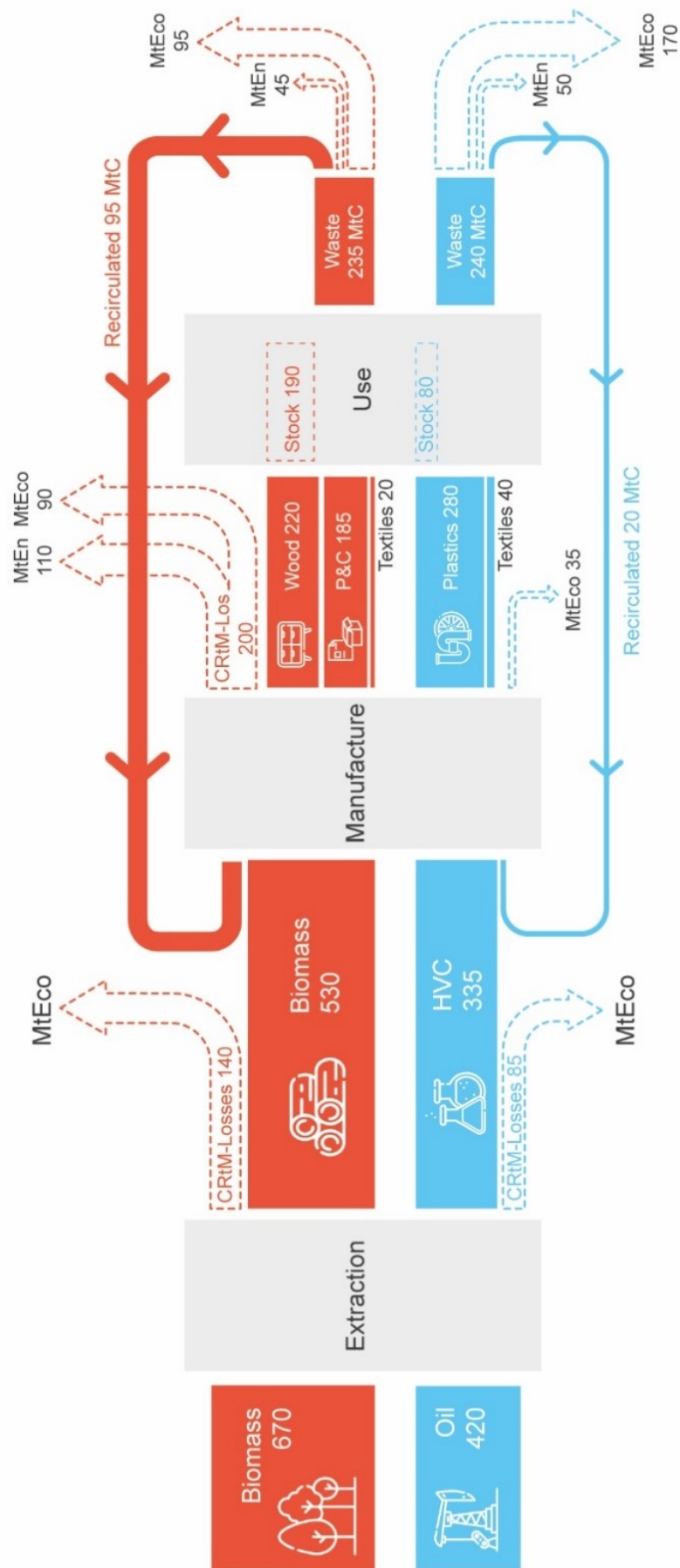
Results for carbon flows

Figure 5 shows the carbon flows of C-Materials for Year 2018. The amount of carbon extracted to produce C-Materials was about 1,090 MtC, consisting of fossil and biogenic resources. On the one hand, 420 MtC of oil were extracted, and about 85 MtC were lost during the transformation processes to produce the base chemicals needed, i.e., 220 MtC of ethylene and propylene, about 100 MtC of BTX, and 15 MtC of methanol. On the other hand, 670 MtC of biomass were harvested, of which 530 MtC were used for materials 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 *Manufacturing* process, representing about 200 MtC of losses of natural C-Materials and 35 MtC of losses of synthetic C-Materials. Of the losses of natural C-Materials, 110 MtC were sent to energy production (MtEn), mainly to the pulp and paper industry to meet internal process energy needs and some wood by-products used as fuels. The remaining 90 MtC were lost to the environment (MtEco).

The total amount of carbon in the C-Materials produced globally was about 745 MtC. Of this amount, 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 their end-of-life the same year, producing a large amount of waste.

The post-consumer waste was estimated at 475 MtC, with similar shares of natural and synthetic materials. Overall, 235 MtC were post-consumer waste of natural C-Materials, of which 45 MtC were incinerated with energy recovery and 95 MtC were re-circulated 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 of these wastes ended up as MtEco (170 MtC), followed by MtEn (50 MtC), and only 20 MtC were re-circulated back to the *Manufacturing* 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 with quality levels similar to those of the original material [42,60].



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

Figure 5. Current C-Material System (from Paper II).

What can we deduce from the carbon flows?

A few observations can be made from the MFA of the current worldwide C-Materials system:

- It is evident that the use and production of C-Materials come with losses. About 815 MtC were lost from the C-Materials system, which is greater than the total amount of C-Materials produced (about 745 MtC).
- Assuming that all 815 MtC of lost carbon ends up as CO₂, this will correspond to the emission of about 3 GtCO₂ from the C-Materials system. This will be equivalent to 6% of GHG emissions, including land use[61].
- The amount of carbon available in waste alone, about 475 MtC, is greater than the amount of carbon needed for synthetic C-Materials production, which is 335 MtC of HVCs. This remains true if we subtract the already re-circulated waste, which corresponds to 115 MtC. Thus, there are still 360 MtC available in the waste to be re-circulated and to produce synthetic materials.

Decoupling from fossil fuels extraction

Post-consumer waste carbon can be re-circulated to produce synthetic C-Materials. In this way, one can avoid emissions, as well as promote de-coupling from fossil fuel extraction.

The MFA showed that the amount of carbon needed to produce plastics is approximately 335 MtC in HVCs and methanol. These chemicals can be produced via feedstock recycling of polymers.

As mentioned in the *Background* section, **Paper I** describes three complementary recycling routes: direct recovery of monomers, syngas synthesis, and combustion with CO₂ recovery. That paper also demonstrates that a combination of these three options can achieve 100% carbon recovery, via the synthesis of syngas and CO₂ to methanol, with the addition of H₂, and thereafter producing methanol to olefins (MTO).

Thus, assuming 100% carbon recovery of the feedstock, we can implement this set of processes in the MFA to create a scenario in which there is de-coupling from fossil fuel resources.

Towards carbon circularity

Figure 6 depicts a proposed scenario in which the post-consumer waste carbon is re-circulated to produce plastics and synthetic textiles, to promote de-coupling 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 for generating the synthetic C-Materials.

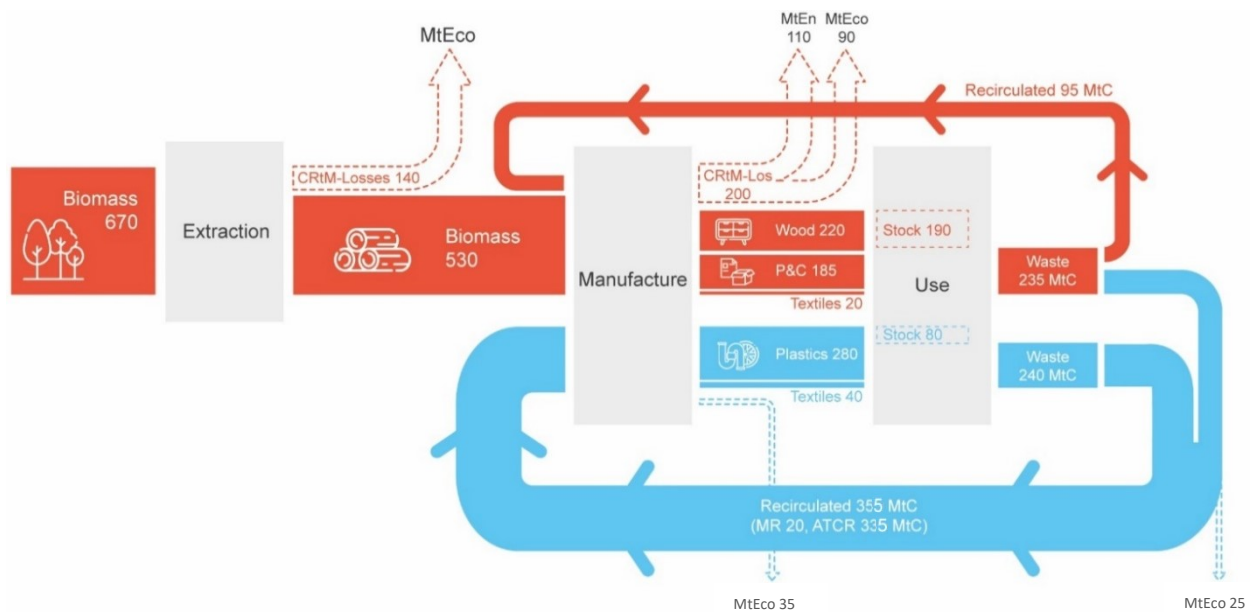


Figure 6. Flow-chart for the proposed re-circulation of waste for a circular C-Materials system.

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.

An important aspect in this scenario is that, the system is de-coupled 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. Note that, in the scenario proposed here, the natural C-Materials part of the system remains unaffected.

Under these conditions, the total losses decrease from 815 MtC to 395 MtC. Assuming once again that the carbon ends up as CO₂, the emissions will be decreased by half, by approximately 1.5 GtCO₂ or 3% of global emissions. These discharges consist almost exclusively of bio-based carbon, which with appropriate management practices, can be considered to be carbon-neutral.

Waste available

If we look more closely at the re-circulated waste in the proposed scenario, we see that from the 335 MtC that are sent to produce HVCs, 120 MtC are from natural C-Materials, and only 215 MtC are from synthetic C-Materials. In other words, about one-third of the carbon will be biomass-based waste, and only about two-thirds of the carbon will be polymers with molecular structures similar to those of the HCVs.

Figure 7 shows the total amount of waste (first top bar), and how much is of natural and synthetic origin (red and blue, respectively), which corresponds to approximately half shares. It also shows what is already being treated with current recycling techniques: about 20 MtC of PET and some PO plastic undergoing solvolysis and mechanical recycling, and mostly paper and cardboard through pulp recycling for the 95 MtC of natural C-Materials re-circulated globally. Thus, the remainder is what can potentially be used for thermochemical recycling processes.

This waste projection helps us not only to know the carbon flows, but also which type of materials we should recycle and how much. If we focus on available synthetic waste, we can see that the plastics that are ‘easily’ decomposable thermally into ethylene and propylene, such as PE and PP, only account for about one-third of the carbon. There is strong interest in developing recycling techniques for these types of plastics. Most techniques focus on packaging and clean/single streams plastics. While most of the PE/PP in waste arises from packaging, in single-material streams, such as bottles, trays and films, a significant fraction is found in blended applications.

A common example is the carton packages used for food and drinks, such as milk and yoghurt, which consist of paper and PE and often contain aluminium foils. However, there are also other multi-layer flexible packaging forms that contain PE/PP and adhesives, as well as PET layers. In addition, PE/PP is not only found in packaging but in multiple applications. For example, cables are composed of polymers such as PE, cross-linked polyethylene (PEX) and PVC, which is a mixture that cannot be mechanically recycled. Thus, only a fraction of the PE/PP is found at the preferred level of cleanliness and in the preferred form for mechanical recycling and pyrolysis (to produce oil). Moreover, those two technologies target the same streams.

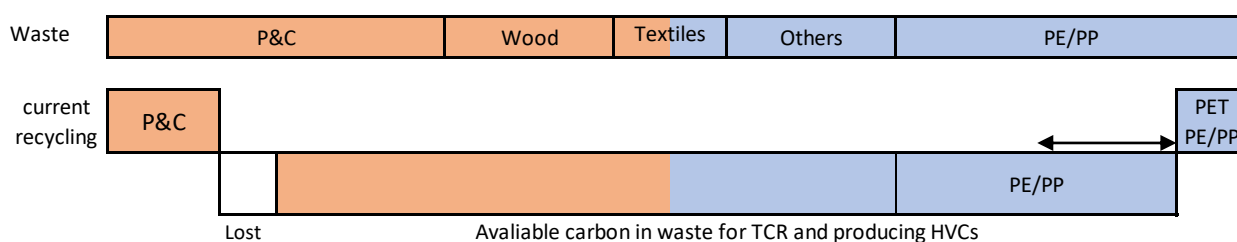


Figure 7. Scheme for available waste on a carbon basis, depicted by type (blue, synthetic C-materials; orange, natural C-materials).

P&C, paper & cardboard; TCR, Thermochemical recycling; HVCs: High Valuable Chemicals.

Most of the available waste is a mix of materials and can be easily blended. Table 2 shows a summary of the available post-consumer flows, categorised according to type of material, and includes their weights on a dry ash-free basis, the total carbon, and their elemental analyses. On a weight basis, the post-consumer waste will consist roughly of 19%wt wood, 23%wt paper and cardboard, 5%wt natural textiles, 9%wt synthetic textiles, and 44%wt plastics. It should be noted that about half of the mass that is re-circulated is natural-based waste, while the other half is synthetic-based. Yet, the carbon contents are different: 47–50%wt for natural C-Materials and 60–80%wt for synthetic materials[62].

Table 2. Estimated wastes available globally in Year 2018 and properties thereof.

Waste	Mt _{daf}	%wt	C _{daf}	H _{daf}	O _{daf}	N _{daf}	S _{daf}	Cl _{daf}	MtC	%C
Wood	102	19	50.3	6.1	43.0	0.4	0.1	<0.1	51	15%
P&C	119	23	46.7	6.2	46.6	0.2	0.2	<0.1	55	17%
Natural TXT	27	5	47.6	6.3	45.1	0.8	0.1	<0.1	13	4%
Plastics*	234	44	79.6	11.3	4.9	0.1	0.2	3.9	186	56%
Synthetic TXT	47	9	59.3	5.3	27.4	7.6	0.5	0.0	28	8%
TOTAL	530		63.1	8.4	25.7	0.9	0.2	1.7	335	

**Comprising 36%PE, 20%PP, 7%PS, 11%PET, 6%PVC, 6%rubber + others*

(carbon contents: for PE/PP, 85-86%wt; for PVC, 40%wt; and for PET 60%wt)

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 CO₂ emissions. An initial observation was that certain aspects need to be considered to convert all the carbon into products, to close the carbon cycle. There are different sources of carbon (natural and synthetic). In addition, the waste contains heteroatoms; here, the projected available waste has about 26%wt oxygen and 3%wt nitrogen, sulphur, and chlorine, so a strategy to deal with heteroatoms is needed.

PART II

Thermochemical recycling of Carbon materials

Thermochemical recycling of mixed C-Materials

The previous section showed that the amount of carbon in post-consumer waste is sufficient for the supply of primary chemicals used for synthetic materials manufacturing, and that the conversion of these materials into valuable chemicals can be achieved via thermochemical recycling. However, it is also illustrated that the available waste is a mix of natural and synthetic C-Materials.

The diverse nature of the waste composition makes it difficult to predict the optimal conditions for the thermochemical recycling process, as the yields are highly dependent upon the molecular structures within the waste stream. Therefore, this section shows the experimental results for the decomposition of mixed waste that mimics the projected available waste.

Waste properties and material content

Five waste fractions, containing different mixtures of C-Materials, were studied. Cable plastic (CP) was studied due to its high polyolefin content and high chlorine (Cl) content, to evaluate the effects of heteroatoms on the conversion process of a waste with a high olefin content. Cardboard recycling residue (CBR) was studied as a mix of bio-based polymers together with PO. Two other wastes were studied due to their highly heterogeneous natures: textiles (TXT); and automotive shredder residue (ASR). TXT and ASR serve as a model for understanding the products obtained from a mixed waste that contains multiple polymers, of both natural and synthetic origin, as well as a significant amount of heteroatoms. In addition, a by-product of the pulp industry, Tall Oil Pitch (TOP) was studied, to represent natural C-Materials that have aliphatic chains that can be decomposed into valuable chemicals, such as ethylene (C₂H₄).

The waste residues have different characteristics in terms of their material and elemental compositions, including heteroatoms. *Table 3* summarises the elemental compositions of the different wastes.

Table 3. Elemental analysis of the mixed wastes tested.

	Tall Oil Pitch (TOP)	Automotive Shredder Residue (ASR)	Cable Plastic (CP)	Textiles (TXT)	Cardboard recycling (CBR)
C (%_{daf})	80.4	66.3	79.2	60.1	66.4
H (%_{daf})	11.1	8.03	11.81	5.44	9.9
N (%_{daf})	<0.01	2.40	0.03	3.85	0.38
S (%_{daf})	<0.02	0.43	0.03	0.16	0.08
Cl (%_{daf})	<1 ppm	1.35**	8.06	0.13*	0.22
O (%_{daf}, by difference)	8.4	21.5	0.9	30.2	23.0
Ash (%_{dry})	0.18	39	28	1.3	8.75

*Includes 0.008% F; **Includes 0.25% Br.

As described in the *Background* section, the products obtained from thermal decomposition reflect the feedstock employed. However, when using mixed waste, it is difficult to define the

material composition. Here, we estimated the polymer content of each mixed waste. The results are based on **Paper VI**, in which the material composition is estimated using the elemental composition of the feedstock and confirmed by the LHV. The most-common polymers, such as PE, PP, PS, PET, PVC, PA, PU and other plastics, together with cellulose and wool were included in the model (for the method employed, see **Paper VI**).

Table 4 shows the materials estimated in the waste samples studied here, divided into six groups of polymer types: polyolefins, PS, PET, PVC, N-containing polymers (PA/PAN/PU), and natural C-Materials, mainly cellulose and wool (Cell/wool). The division was chosen given the different decomposition pathways shown in *Figure 4*. Polyolefins produce light olefins, PS produces both aromatics and olefins, PET also produces aromatics and olefins, as well as oxygenated compounds. PVC and PA/PAN/PU were distinguished based onto their heteroatom contents, Cl and N, respectively. Finally, natural polymers, such as cellulose and wool, reveal how much of the waste is not synthetic C-Materials.

Table 4. Material type estimate for each feedstock (%_{daf}).

	<i>TOP*</i>	ASR	CP	TXT	CBR
P-olefins	55%–66%	32%	80%	-	47%
PS	10%–28%	14%	3%	-	-
PET	0%–25%	-	2%	70%	9%
PVC	-	2%	14%	0.2%	0.4%
PA/PAN/PU	-	23.5%	0.3%	17%	4%
Cell/wool	0%–17%	28.5%	-	13%	39%

**Estimate*

Automotive shredder residue (ASR) is a plastic-rich fraction that is acquired when rejected cars and waste electrical and electronic equipment (WEEE) undergo metal recycling. This fraction is a highly heterogeneous stream that contains a mixture of plastics, as well as wood and textiles with up to 50% inorganics, e.g., fillers, metals, and glass. This waste fraction was studied due to its complex polymer blend and low polyolefin content and the fact that it is rich in ash and heteroatoms.

The method gives an approximation of what these plastics might be. As shown, about 32% of the weight (daf) consists of polyolefins, mostly PP, which is commonly used in cars, from bumpers and insulation to carpet fibres. The second-most-abundant polymer is cellulose, at 28.5%, which is mostly wood, given that older automotive vehicles contain wooden frames. Another common material is PU, at 23.5%, which is used in both soft and hard forms, as in tires, suspensions and seating. Part of that fraction is PA, used for weather/water-proof coating [63]. Another polymer in car parts is polystyrene, here making up 14% of the weight, which originates from high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS). PS is also very commonly used in white goods, which in this case was also sent to the automotive residue recycling process.

Cable plastic (CP) waste is also a left-over fraction, in this case from the recycling of cable metals. Desirable metals are mechanically separated, leaving a shredded plastic fraction. Cable plastic is composed of a blend of polymers: PE, cross-linked polyethylene (PEX), and polyvinyl chloride (PVC). Currently, the mix of PEX and PVC cannot be mechanically recycled. Through thermochemical processes, these polymer chains can be broken into syngas and monomers, which can be used subsequently in the chemical industry. This mix was studied due to its high PO content, as well its high Cl content, to evaluate the fate of Cl and its effect on the product distribution. Table 4 shows that CP is estimated to consist of about 80% polyolefins, 14% PVC, and 6% other species, including a minor fraction of nylon for insulation and some PS and PET, which are commonly found in other electric components (i.e., capacitors).

Textile (TXT) waste is a heterogeneous blend of synthetic and natural C-Materials. Most of the TXT is polyester, while other synthetic textiles, such as nylon, acrylic and elastane, are found in this waste. In addition, significant amounts of cotton and wool, together with artificial cellulosic fibres are present. This waste fraction was studied because of its natural and synthetic polymer blend, low polyolefin content and relatively high N content. About 70% of the TXT is polyester, while other synthetic textiles account for 17% of the weight, including nylon, acrylic and elastane, here represented as PA/PAN/PU. About 13% of the weight is natural materials, i.e., cotton, and wool, together with artificial cellulosic fibres, such as viscose. In addition, about 0.2% is PVC, which is commonly found in water-proof jackets and other clothes.

Cardboard recycling (CBR) residue is also a heterogeneous blend of synthetic and natural C-Materials. However, compared to textiles, it has a high aliphatic content. CBR is a post-consumer waste stream from multi-layer cardboard and plastic packaging, which are used for food that needs a protective layer against the atmosphere (such as milk, yoghurt, etc.). This waste fraction was studied because of its natural and synthetic polymer blend and its rather high polyolefin content, about 47%wt, which comes from the PE layer used to contain liquids, and about 39%wt cardboard, from the outer layer of liquid-containing packaging (e.g., cardboard milk containers). About 9% of the waste is PET, which is also used as a food container layer. About 4% is PU, which can represent adhesives and/or other packaging waste that is inappropriately sorted, and about 0.4% is PVC.

Tall Oil Pitch (TOP) cannot be classified in the same way as the other feedstocks, since it is not a combination of materials but a by-product of biomass processing. TOP consists mainly of free fatty acids and derivatives (40%–50%), resin acids (20%–25%), and unsaponifiables (30%–35%). A fatty acid is a carboxylic acid ($R-COOH$) with an aliphatic chain that contains from 4 to 28 carbons. It resembles polyolefins. TOP was added to the model to identify materials to which it would correspond. The model gave two possible solutions, one with 64% PE, 10% PS and 25% PET, and the other with 55% PE, 17% cellulose and 28% PS. Both solutions give a similar profile, with a high content of aliphatics and some aromatic and oxygenated compounds.

C-bond estimate

An in-depth analysis of the composition can be carried out by focusing on the bonds contained in each plastic, such as aliphatic bonds, aromatic bonds or bonds with oxygen or other heteroatoms. Thus, in **Paper IV**, each plastic was classified according to its aliphatic chains and aromatics (C-AL and C-AR, respectively), as well as with heteroatoms, here divided into C-O and C-X, with the latter including N and Cl. For instance, PE and PP have all their C-bonds in aliphatic form, while PAN has two-thirds of its carbon as C-AL and one-third with N, as C-X. PS and PET have most of their carbon as C-AR, with some as C-AL and C-O, correspondingly.

Given the polymer type estimated for each feedstock and the carbon bond definition (see **Paper IV**), we can calculate the total amounts of bonds with Oxygen (C-O), aliphatic and aromatics for each waste, as well as with other heteroatoms. Table 5 shows the percentage of carbon for each bond for the studied feedstocks.

Table 5. Carbon bond estimates for each feedstock (%_{daf}).

	C-O	C-AL	C-AR	C-X
TOP*	10–13	65–67	22–23	0.0
ASR	21.0	43.3	29.9	5.8
CP	0.9	91.9	3.8	3.4
TXT	37.1	14.3	44.4	4.2
CBR	26.0	66.0	7.8	0.1

**Estimate*

The results are in line with the material composition. The most interesting is TOP, in that even the material estimate analysis gave two possible solutions, and the carbon bond results give very similar percentages.

Both the material types and the carbon bond estimates are useful for obtaining a full picture of the product distribution following the steam cracking of these feedstocks, which will be presented shortly.

Experimental set-up

The technology to be employed was chosen based on the requirements that the process must: (i) be capable of handling diverse types of waste mixtures; and (ii) be able to provide high heat transfer and high temperatures (700°–850°C). In addition, to avoid the production of undesired secondary reactions at high temperatures, 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 [64].

Among the different thermochemical methods studied previously, the Fluidised Bed (FB) concept has proven to be suitable for non-homogeneous fuels, such as waste fractions that have low heat conductivity and materials with high plastics content [65–67].

The experiments were performed in the Chalmers Research Unit, which houses a 10–12-MW_{th} circulating fluidised bed boiler and a 2–4-MW_{th} bubbling bed steam cracker, which allow feeding rates of 50–300 kg/h. A schematic of the Chalmers' Dual Fluidised Bed (DFB) unit is shown in *Figure 8*. The DFB system comprises two connected reactors, a combustor (2) and a reactor (6), here referred to as a *steam cracker*. A looped, sand-like bed material with high heat transfer capability acts as the heat carrier for 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 with wood chips and wood pellets (1), whereas the gasifier is fluidised with steam and fed mixed waste (8). In the present study, silica and olivine sand were used as the bed materials that provided heat transport between the reactors.

Three different feeding techniques were used to adapt the system to the waste stream: (i) a liquid feeding with a heated line for TOP (marked with a triangle in *Figure 8*), given that is a highly viscous liquid; (ii) a pellet screw feeder for ASR, CP and TXT with flow rate in the range of 100–300 kg/h; and (iii) a new feeding system installed in Year 2020 that consists of an extruder with a feeding rate in the range of 30 –120 kg/h was used for processing the CBR. The extruder (partially) melts the waste and is fed from the top the loop seal 1 (5) indicated in the scheme, right before the steam cracker reactor.

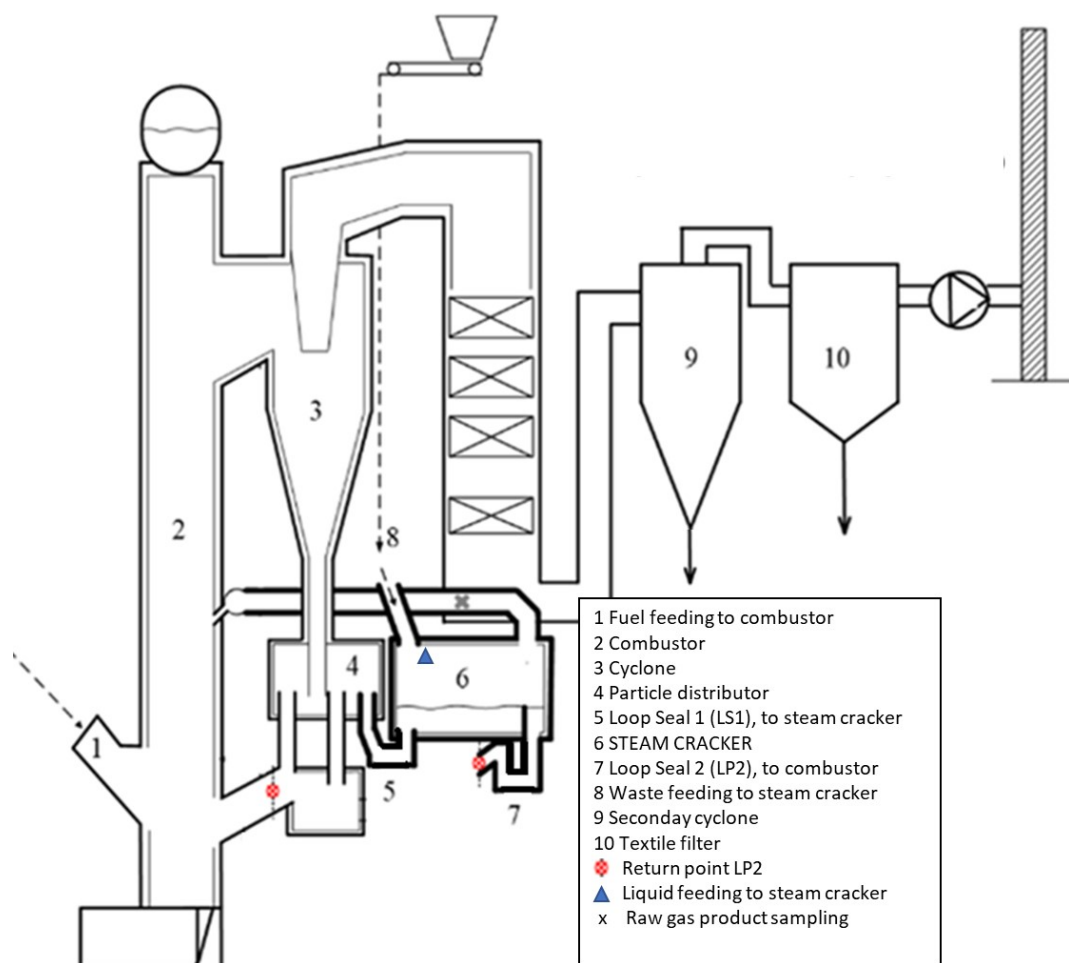


Figure 8. Schematic of the Chalmers' DFB unit.

The circulating fluidised bed boiler comprises the combustor (2) 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 steam cracker (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 (1) and steam cracker (8) are indicated by arrows. Lastly, the raw gas is fed to the boiler.

Product sampling and measurements

The experimental results are presented chronologically: TOP, ASR, CP, TXT and CBR. The reason for this is to follow the time-line of the measurement techniques, which progressively improved the understanding of the product distributions from the steam cracking processes for these waste streams. In addition, in Year 2020, a new extruder feeder was implemented to feed plastics into the reactor.

The decomposition of the feedstock can be divided into the devolatilized products and non-fully devolatilized feedstock. The process performance was evaluated through characterization of the raw gas produced in the steam cracker. For all the samplings, gas streams were extracted from the sampling point (cross symbol *Figure 8*) and analysed after particle removal with a high-temperature filter (set at 350°C, with a mesh of 2 micrometres). Helium was added to the process as a tracer gas, to determine the gases produced, and the measurements were made during stable operation.

The measurement techniques were improved with time, marked in blue. Table 6 shows which technique was used for each waste.

Table 6. List of feedstocks and their measurement techniques for the industrial

Measurement technique	TOP	ASR	CP*	TXT	CBR
Micro-GC	X	X	X	X	X
SPA	X	X + N-arom	X + N-arom	X + N-arom	X
HTR		X	X	X	X
Double SPA				X	X
GC-MS		X**	X**	X**	
GC-VUV					X

***performed later. *repetition in lab scale including Double SPA and m-GC for C4-C5s*

In the first sampling stream, the permanent gases were analysed by gas chromatography (GC), after quenching and removal of particles and water. A **micro-GC** (GC-TCD - Varian CP490) was employed, which was calibrated for He, H₂, CO₂, CO, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, O₂ and N₂. The aromatics fraction was sampled using solid-phase adsorption (**SPA**) [68] and analysed (four repetitions per sampling point) using a GC-flame ionization detector (GC-FID - Bruker GC-430). Thirty compounds, with boiling points in the range of those of benzene and coronene (C₆H₆ and C₁₈H₂₂), were calibrated and quantified (see Table 7).

For TOP, ASR and CP, the SPA method was performed using one amine for the absorption of the aromatics fraction. The analyses showed high variability of the benzene content between samples. At the same time, the non-identified fraction was relatively large compared to other experiments. Thus, additional method development was carried out by conducting laboratory tests to improve the absorption. As sampling with SPA is sensitive to high concentration levels in the raw gas, the degrees of absorption of benzene and toluene were improved. Thus, for TXT and CBR, the aromatics were measured using the SPA method with two amines (**double SPA**) for the adsorption (instead of one).

In addition, given the high concentration of N in textiles, three N-containing compounds were calibrated, namely aniline, benzonitrile and p-toluidine, after the textile experiments (**N-arom**). While the calibrations of these compounds were performed in 2020–2021 for TXT, they were included a posteriori for ASR and CP.

To extend the characterization of the aromatic products, some of the samples underwent further analyses. The non-calibrated aromatics in the SPA were identified and estimated using **GC-MS** for ASR, CP and TXT. The aims were to study in detail the carbon distribution and to investigate the heteroatoms in that fraction. The GC-MS-estimated aromatics comprised compounds with carbon numbers from C₆–C₂₂. For the GC-MS analysis, results with a NIST fit >80% were considered reliable, and those with NIST fit between 70% and 79% were deemed to be correct [69].

Table 7. Measured aromatic compounds, including those calibrated and identified.

Group	Aromatic compounds
Benzene	Benzene*
Toluene	Toluene*
Xylene	o-xylene*, p-xylene *
Styrene	Styrene*, methyl-styrene *
1-ring	Other 1-ring aromatics identified with the GC-MS
Naphthalene	Naphthalene*, 1,2-dihydronaphthalene*, 1-methylnaphthalene*, 2-methylnaphthalene*
2-ring	Indene*, biphenyl* and other 2-ring aromatics identified by GC-MS
≥3-ring	Acenaphthylene*, acenaphthene*, fluorene*, phenanthrene*, anthracene*, xanthene*, fluoranthene*, pyrene*, chrysene* and other ≥3-ring aromatics identified by GC-MS
Oxygenated	Phenol*, o/p-cresol*, 1-naphtol*, 2-naphtol*, benzofuran*, dibenzofuran* and other oxygenated aromatics identified by GC-MS
Nitrogenated	Aniline*, benzonitrile*, p-toluidine* and other nitrogenated aromatics identified by GC-MS

**Calibrated compounds.*

In the second sampling stream, all the products were cracked in a High-Temperature Reactor (**HTR**) at 1,700°C, thereby cracking the present hydrocarbons to form H₂, CO, CO₂, and H₂O. The steam was condensed, and the dry gas was analysed in a micro-GC[67]. The **HTR** aids assessment of how much of the fuel can be found in the gas and allows for establishing a carbon balance over the steam cracker. The total carbon in the gas was assessed with the **HTR**. The products that remained in the bed were non-fully devolatilized feedstock and their levels were calculated by the difference between the fuel input and the **HTR** carbon output. Comparison of the results from the first and the second sampling streams were used to identify gaps in the species analysis. This tool was available for all the experiments, with the exception of the TOP analysis.

Initially, only light hydrocarbons, i.e., C₂–C₃s were measured using the above-mentioned **GC**, although other linear hydrocarbons were produced. For the last experiments with CBR, Gas Chromatography – Vacuum Ultraviolet Spectroscopy (**GC-VUV**) was implemented to measure the levels of linear and cyclic C₄–C₅ hydrocarbons [70].

Results from steam cracking of mixed waste

In this section, the experimental test results are summarised. The main products and the carbon balance are shown at two different temperatures for each waste. The parameter of temperature was chosen because it has the greatest effect on product distribution, as demonstrated in **Paper IV**.

The wastes are presented in chronological order, to show the improvements that occurred in the measurements. The product distribution is colour-coded according to the following temperature ranges: white, 730°–740°C; grey, 775°–800°C; and black, >800°C. The carbon balance indicates with different shades of green the products that are HVCs, namely ethylene, propylene, BTX, and C4-5 hydrocarbons.

Tall Oil Pitch (TOP)

Tall oil pitch was tested at 775°C and 825°C. Liquid feeding was at 175 kg/h and 150 kg/h at the low and high temperatures, respectively. The steam flow was 160 kg/h for both cases and silica sand was used as the bed material. These results are taken from **Paper III**.

The measurement systems used for these experiments had some limitations. The method used was **micro-CG**, which included syngas, here defined as H_2 , CO , CO_2 and CH_4 and C2–C3 hydrocarbons (C_2H_4 , C_2H_2 , C_2H_6 , C_3H_6 and C_3H_8), and **SPA** with one amine, which has shown a limited ability to capture all of the benzene and toluene. In addition, the HTR was not accessible, and the total carbon converted was not analysed. Another limitation was the lack of analysis of other linear hydrocarbons, such as the C4–C5 compounds.

In Figure 9, the molar yields of the measured gases are shown for the two temperatures investigated. It is evident that the steam cracking of TOP produced a significant amount of syngas (H_2 , CO , CO_2 and CH_4). There was also high-level production of C_2H_4 and rather high levels of formation of aromatic compounds, at 2 mol/kg_{daf}, which corresponds to about 190 g/kg of TOP.

Temperature plays an important role in decomposition. The results for TOP in Figure 10 show that a higher temperature led to increased levels of most of the gases produced (H_2 , CO , CO_2 , CH_4 and C_2H_4). In particular, at 825°C, the total gas yield was about 10% higher than at 775°C. The highest increases in yield with temperature were observed for CO_2 and C_2H_4 (30% and 20% increases, respectively), while the yields of other C2–C3 hydrocarbons showed a 20% decrease with the increment of temperature.

The measured aromatic yields are also depicted in Figure 9. Increasing the temperature resulted in an increase in the levels of PAH compounds, while the yield of mono-aromatics appeared to decrease. At 775°C, the levels of Benzene, Toluene, Xylene and Styrene (BTXS) were higher. However, given the limitation of the SPA method, this result cannot be corroborated.

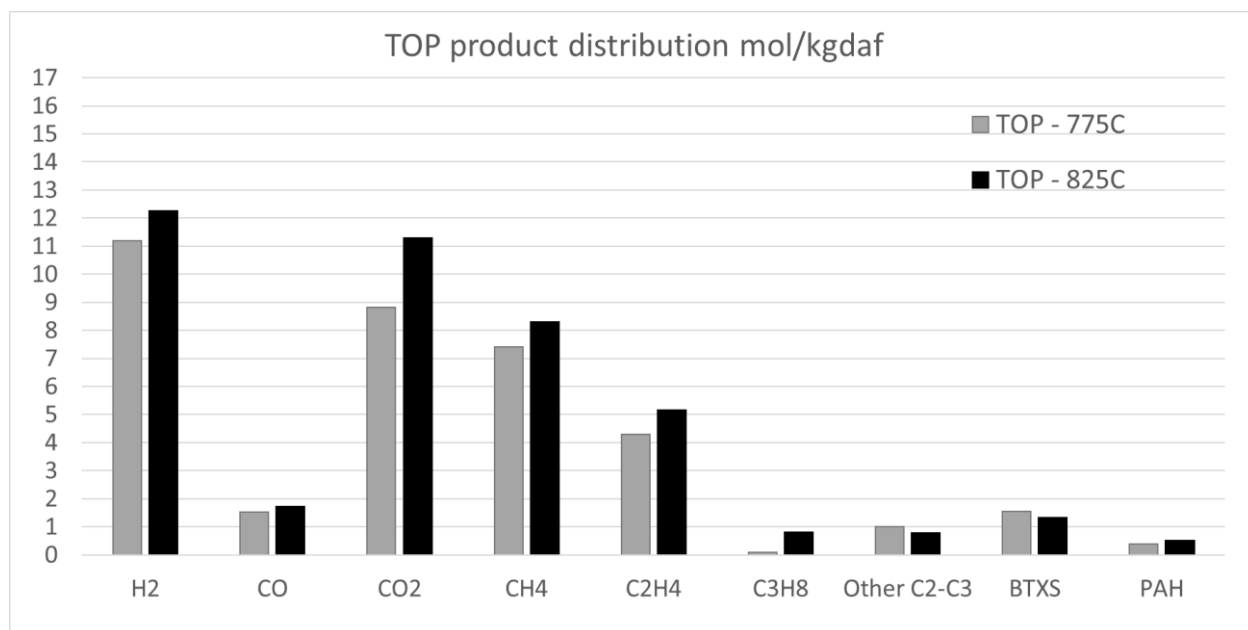


Figure 9. TOP product distribution from steam cracking (mol/kg_{daf})

The carbon distributions of the products leaving the cracker are shown in Figure 10, providing a clearer picture of the product distribution. The products are lumped into five categories: CO_x; CH₄; C₂–C₃ hydrocarbons; BTXS and PAH.

The percentages of carbon in the form of CO_x were 15%C at 775°C and 19%C at 825°C. Concerning the measured aliphatic products, 11%C and 12%C was found in form of methane, at low and high temperatures respectively. The C₂–C₃ products had a similar amount of carbon in this form (about 21%C) at the temperatures studied. A similar trend was observed for the aromatics fraction, with TOP yields of about 20%–21%C in aromatics compounds. For both cases, BTXS were the main compounds, accounting for 13–15%C, and the PAH are 5–8%C, showing that increasing the temperature leads to poly-aromatisation.

A significant amount of carbon was unidentified and/or non-fully devolatilized feedstock. The carbon contents were 32%C and 26%C at the low and high temperatures, respectively. While the presence of some non-fully devolatilised feedstock or char was possible, this seemed unlikely because the feed was in liquid form and the feedstock contained only around 1%C of fixed carbon (FC), which meant that only a small fraction of char could be expected. It was speculated that this was mostly an unidentified fraction, consisting of unmeasured hydrocarbon species.

This fraction may be unidentified hydrocarbons of the forms C₄–C₆, both linear and cyclic, which have H/C ratios between 1.5 and 2.5. This fraction is likely given that almost 70% of the carbon bonds in TOP were estimated to be C–Al. In addition, the unidentified compounds could be benzene and toluene, given the limitations of the SPA method employed in these experiments, as well as the high percentage of C–AR in TOP. Another option is soot, here defined as PAH with C>18 and particles formed from the inception and aggregation of PAH, with H/C ratio close to 0.

The hydrogen balance was investigated to gain further insights into the content of the unidentified fraction (for the calculation, see **Paper III**). The H/C ratio of the unidentified fractions was estimated to be between 0.7 and 2.1 at 775°C, and between 0.5 and 2.8 at 825°C.

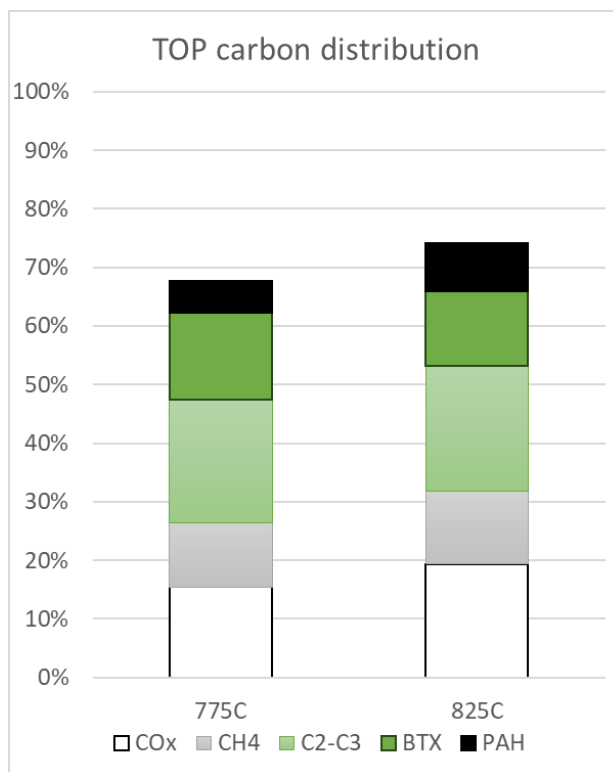


Figure 10. Carbon distribution from steam cracking of TOP

Previous research has shown that at 775°C, there is a significant presence of C4–C6 linear hydrocarbons and a low level of soot formation. Mandviwala et al. have reported 5%C as C4 hydrocarbon during steam cracking of rapeseed oil at 750°C in a laboratory FB, with about 18%C BTXS and also 6%C not detected, which was speculated to be C5–C6 hydrocarbons [71]. Given the similarities between rapeseed oil and TOP, with both containing fatty acids, the presence of C4–C6 hydrocarbons, both linear and cyclic, is likely. In addition, the range of the H/C ratios of the unidentified fraction supports this possibility, since the H/C ratio can reach up to 2.1.

Nonetheless, the lower minimum H/C ratio is 0.7, which suggests that some more BTXS and some soot may be formed. The same study [71] showed about 20% more BTXS formation for rapeseed oil than for TOP, which indicates that more BTXS was formed than was measured, given that TOP is about 50% fatty acids, which are aliphatic chains that can lead to aromatics, and the remainder is resin acids and unsaponifiables. In addition, the rapeseed oil gave <2%C of soot and 5%C of PAH at 750°C. Therefore, it seems likely that most of the unidentified products (32%C) are cyclic and linear C4–C6 hydrocarbons, including BTXS, and that a small amount of soot is formed during TOP decomposition at 775°C.

At 825°C, the cracking severity increases, thereby decreasing the quantity of C3 hydrocarbons in the products. Thus, it can be expected to have fewer linear C4–C6 hydrocarbons at 825°C

than at 775°C, as we have seen with the decrease in the levels of other C2–C3 when increasing the temperature (Figure 9). In other words, the presence of C4–C6 hydrocarbons at 825°C is possible but the levels are lower than at 775°C, which is corroborated by the finding of lower levels of unidentified species (26%C at 825°C, as compared to 32%C at 775°C).

Considering the H/C ratio, the theoretical maximum H/C ratio (i.e., H/C ratio of 2.8) for TOP products is unlikely to be due to an increase in cracking severity, given that the linear hydrocarbons have H/C ratios of between 1.5 and 2.5. On the contrary, the minimum H/C ratio is lower at high temperatures than at low temperatures, which points towards more BTXS and soot formation. In addition, an increase in PAH was observed at 825°C, so more soot was likely formed at a temperature higher than 775°C.

Increasing the severity results in different heteroatom concentrations in the gas compared to in the aromatics fraction. As shown in Table 3, the main heteroatom in TOP is oxygen (about 8%_{daf}). While most of the oxygen ends up as CO and CO₂, a small percentage remains in the aromatics fraction. At 775°C, 0.35% of the oxygen in TOP is found in the aromatics, while at 825°C, only 0.05% of the oxygen in TOP is found in the aromatics.

Automotive Shredder Residue (ASR)

The ASR was tested at multiple temperatures and under different conditions (see **Paper IV**), although the results for only two process temperatures (790°C and 835°C) are described here, to exemplify the distributions. The screw feeder was operated at a feeding rate of 155 kg_{daf}/h, and the steam flow was 160 kg/h for both cases. Olivine was used as the bed material. These results are taken from **Paper IV**.

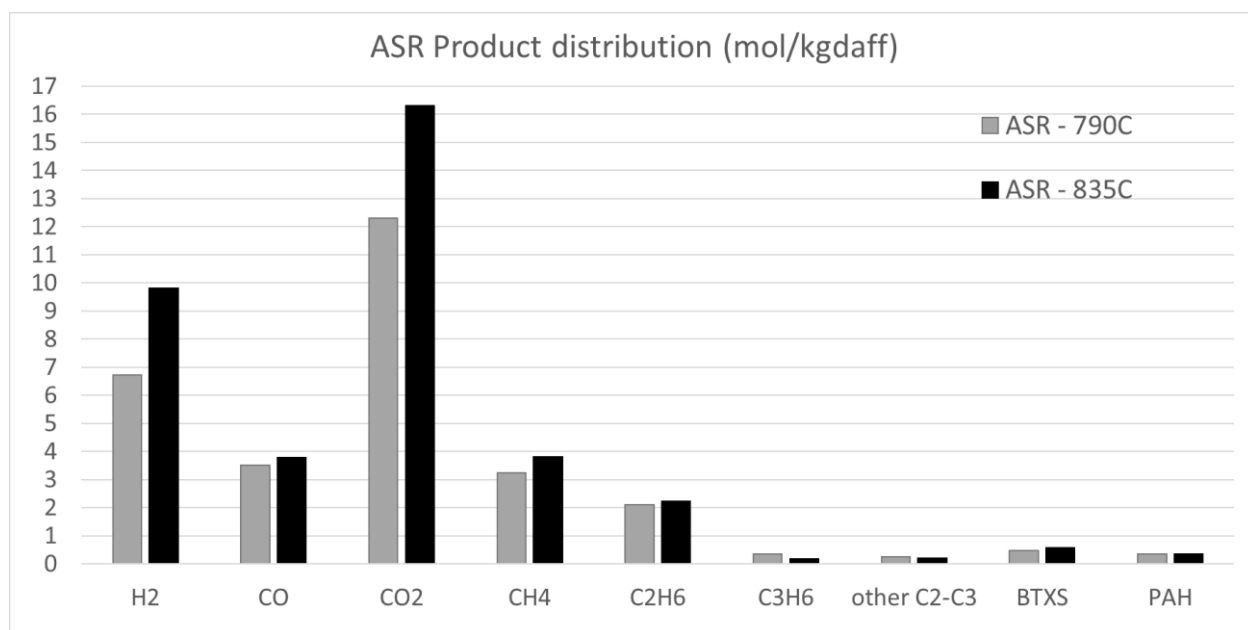


Figure 11. ASR product distribution from steam cracking (mol/kg_{daf}).

The measurement systems used for these experiments were the same as for TOP. The method used was **micro-CG** (including syngas and C2–C3 hydrocarbons) and **SPA** with one amine, which limited the capability to capture all of the benzene and toluene. In this case, the total carbon converted was analysed using the **HTR**. Thus, the main limitations were the analysis of benzene/toluene and the lack of detection of linear C4–C5 hydrocarbons.

Figure 11 shows the measured gases from steam cracking of ASR (in mol/kg_{daf}) at the two temperatures. The most-abundant product was syngas, for which the yields increased with increasing temperature; in particular, the H₂ and CO₂ yields increased significantly, and the yield of CH₄ showed a moderate increase. The yield of C₂H₄ increased only slightly, and the yields of C₃H₆ and the other C2–C3 species decreased when the temperature was increased from 790°C to 835°C.

Overall, slightly lower concentrations of aromatic compounds were detected at 790°C than at 835°C (0.8 mol/kg_{daf} vs. 0.9 mol/kg_{daf}). The main products in the aromatics fraction were BTXS, the levels of which increased slightly with temperature, although as explained above, benzene and toluene may have been under-represented. There was also a slight increase in the levels of PAHs with increasing temperature.

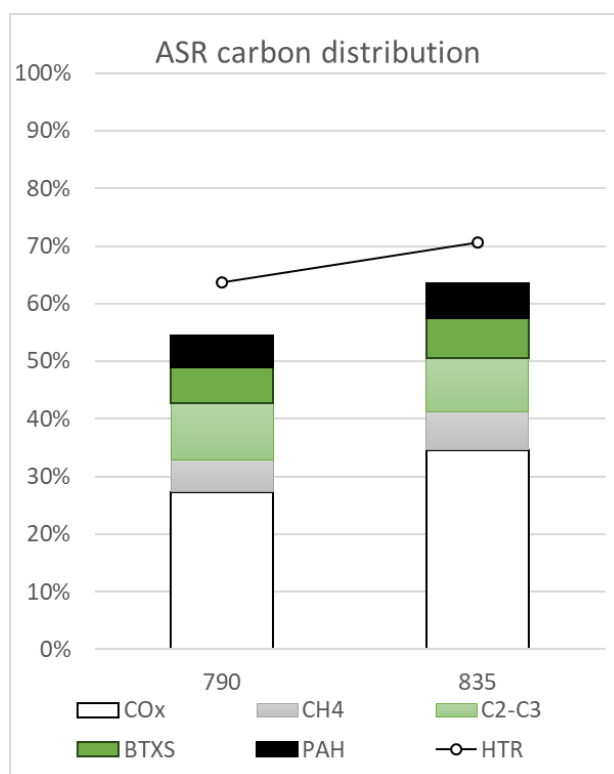


Figure 12. Carbon distribution from steam cracking of ASR

The carbon distributions of the products leaving the cracker are shown in Figure 12, where 100% corresponds to the total carbon in the ASR. The products are divided into five categories: COx, CH₄, C2–C3 hydrocarbons, BTXS, PAH. In addition, the total carbon measured in the gas with the HTR is depicted with a line.

The percentages of carbon in the form of CO_x were 27%C at 790°C and 35%C at 835°C. Concerning the aliphatic products, methane was about 6%C and 7%C, and the C₂–C₃ fraction, ASR showed similar amounts of carbon in this form 10%C and 9%C, at the low and high temperatures, correspondingly. A similar trend was observed for the aromatics fraction, with ASR yields of about 12–13%C. For both cases, BTXS are the main compounds, accounting for 6–7%C, and the PAHs accounted for 6%C.

The total carbon in the gas measured in the HTR was 64% and 71%, at 790°C and 835°C, which is relatively small, suggests a large fraction of non-fully devolatilized feedstock. The gap between the quantified carbon products (CO_x, CH₄, C₂–C₃ and aromatics) and the total carbon measured with the HTR, i.e., unidentified carbon products, were 9% and 7%C at the low and high temperatures, respectively, which likely consists of unmeasured hydrocarbon species.

This unidentified fraction might be linear C₄–C₆ hydrocarbons and aromatics, benzene and toluene. However, given the low concentrations of C₂–C₃ aliphatic compounds, in particular, C₃ (only 1–2%C), it is possible that the levels of other linear hydrocarbons are not significant. The estimated H/C ratio of this unidentified fraction was around 1.3 for both cases. This together with the fact that benzene and toluene were under-measured, suggests that the missing carbon is mostly benzene and only a small fraction is C₄–C₅ hydrocarbons. In addition, the unidentified compounds could, in part, be soot (PAHs >C₁₈).

The measured aromatics were only 12–13%C, while about 30%C in the fuel was aromatics bonds (C-AR). Thus, it can be expected that more aromatics were formed. While we cannot know about the additional benzene and toluene produced, we can have a better understanding of the unidentified species by examining the GC-MS spectra of the aromatic fraction samples (SPA).

Starting with the PAHs, it was estimated that less than 2%C was in the form of aromatics with three or more cyclic/rings. Furthermore, only a few compounds >C₁₈ were found, and the highest was C₂₀H₁₀. Denoting that a limited growth of the PAHs can be expected.

Other unidentified or non-measured compound are hydrocarbons containing heteroatoms. ASR contains 2.4%_{daf} of nitrogen and the GC-MS analysis detected many aromatic compounds that contained N. The calibrated compounds (aniline, benzonitrile and p-toluidine) were identified and measured, and other N-containing compounds were detected in the GC-MS, with -CN and -NH₂ radicals. About 6% of the N content (%N) was detected in the aromatics at 790°C and only 3%N was detected at 835°C, indicting a decrease when increasing the severity. Of the detected compounds, around 70% were the calibrated compounds (aniline, benzonitrile and p-toluidine), and the remainder was estimated from the GC-MS results.

The detected N-aromatics accounted for about 1%C. Given that ASR contains rubbers and polyamides, it is possible that other N-containing compounds were produced. As explained before, these polymers can decompose into NH₃, HCN, acetonitrile, acrylonitrile and propionitrile under the conditions studied here. If the remaining N was found as HCN, it would

correspond to 3%C. Similarly, it would correspond to 6%C if it was found as C_2H_3N , or 9%C if it was found as C_3H_5N . Therefore, a few percentages of carbon in the unidentified fraction can be expected in the form of non-measured N-compounds.

Regarding other heteroatoms, ASR contains some sulphur (S), chlorine (Cl) and bromine (Br), as well as a considerable amount of oxygen in the feedstock. When it comes to oxygen, in similarity to the TOP, the ASR oxygen ends up mostly as CO and CO_2 , and a small fraction appears in the aromatics. About 0.8% of the oxygen is found in the aromatics at 790°C and only 0.3% at 835°C.

All of the S ended up as H_2S at 835°C. In contrast, only about 40% of the S was found as H_2S at 790°C, and about 10% of the S was found in the aromatics fraction.

Chlorinated hydrocarbons were not detected in the GC-MS, but two brominated compounds (CBr_3F and $C_{13}H_9Br$) were detected at 790°C, accounting for about 3% of the Br in the fuel.

Cable plastic (CP)

The CP was tested at two temperatures, 735°C and 800°C. The screw feeder was used, at feed rates of about 120 kg_{daf}/h and 100 kg_{daf}/h at the low and high temperatures, respectively. The steam flows were 160 kg/h at 735°C and 130 kg/h at 800°C, and silica sand as bed material. These results are taken from **Paper V**.

The measurement systems used for these experiments were the same as for the ASR. The methods used were **micro-CG** (including syngas and C2–C3 hydrocarbons) and **SPA** with one amine for the aromatics, and **HTR** for the total carbon converted. Again, the main limitations were the analysis of benzene/toluene and linear C4–C5 hydrocarbons.

Figure 13 shows the gas distributions from steam cracking of CP (in mol/kg_{daf}) for the two temperatures at the industrial scale. The most-abundant gas products were H_2 , CH_4 , and C_2H_4 , for which the yields increased with the increase in temperature from 735°C to 800°C.

The operational temperature of 735°C seemed to favour the formation of propylene, and other C2–C3 hydrocarbons, whereas the yields of H_2 , CH_4 , and C_2H_4 were lower than at the higher temperature. When it comes to oxygenated compounds, we found similar concentrations of CO_2 under the conditions studied here. In contrast, the CO yield almost doubled with the increase in temperature from 735°C to 800°C.

Overall, lower concentrations of the measured aromatic compounds were seen at 735°C than at 800°C (0.8 mol/kg_{daf} vs. 1.2 mol/kg_{daf}). The main products in the aromatic fraction were BTXS, which removes uncertainties regarding the measurement of benzene and toluene. There was also a clear increase in the levels of PAHs with the increase in temperature from 735°C to 800°C.

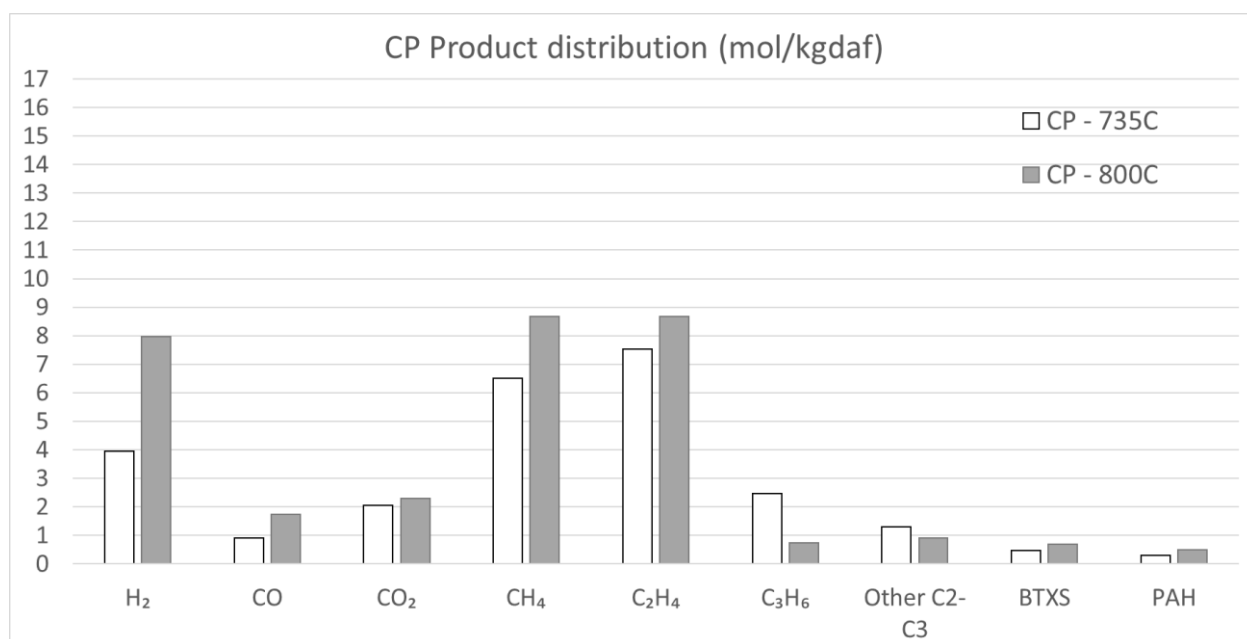


Figure 13. CP product distribution from steam cracking (mol/kg_{daf})

As mentioned above, the samples displayed high variability with regards to benzene, suggesting insufficient absorption by the SPA due to high concentrations in the sampled gas. Similarly, the level of toluene is uncertain due to the high variability observed under both temperatures.

The carbon distributions of the products leaving the cracker are shown in Figure 14. The products are divided into five categories: CO_x, CH₄, C₂–C₃ hydrocarbons, BTXS and PAHs. The total carbon measured in the gas with the HTR is depicted with a line.

Overall, the total carbon measured in the gas with the HTR varied substantially at the different temperatures. At 735°C, the overall carbon conversion was about 76%C, whereas at 800°C, it was around 90%C. As observed, the carbon contents of the CO_x increased with temperature, from 5%C to 8%. The carbon contents of CH₄ also increased, from 10%C to 13%C, while C₂–C₃ hydrocarbons decreased moderately with temperature, from 38%C to approximately 32%C. Similarly, the total aromatics measured (BTXS and PAHs) was 8%C and 13%C, at 735°C and 800°C, respectively.

The quantified carbon products with the measurements available in the industrial plant tests added up to 61%C and 66%C, leaving a significant amount of unidentified carbon products. 16%C and 26%C at the low and high temperatures, respectively, which likely consists of unmeasured hydrocarbon species.

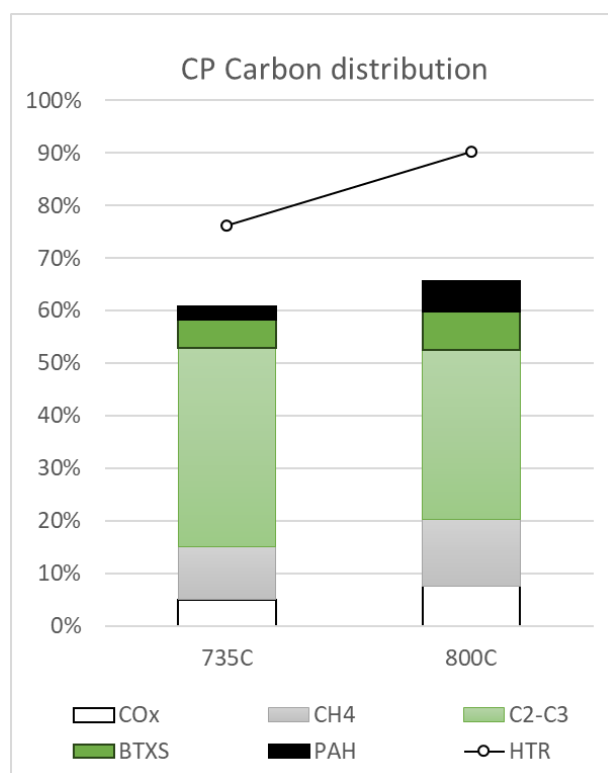


Figure 14. Carbon distribution from steam cracking of CP

Given that CP is a highly aliphatic feedstock, additional experiments were performed on a laboratory scale to include the full analysis of BTXS and of the linear hydrocarbons (see Paper V). The C4–C5 hydrocarbons were included in the measurements, using another micro-GC[72]. The full extent of the BTXS formation was analysed using the double SPA method.

The concentrations of C4–C5 hydrocarbons and BTXS measured in the laboratory were very different to those at the industrial site. C4–C5 compounds were measured in the laboratory, showing a substantial amount of carbon in those products as well as a stiff decrease with temperature, from 13%C to 2%C. In addition, the BTXS aromatics measured in the laboratory with the **double SPA** method showed higher levels of formation of BTXS, about 18%C, consisting mostly of benzene, at both temperatures, as compared to the 5%C and 7%C measured in the plant.

The laboratory results contribute to explaining the unidentified fraction at the industrial site, which corresponds to 16%C at 735°C. This fraction can be explained by the C4–C5 hydrocarbon fraction, 13%C in the laboratory, and total BTXS measured in the laboratory, 12% points higher than the measured in the industrial site. In addition, performing a hydrogen balance over the products in the industrial site indicates that the unidentified fraction at 735°C has an H/C ratio of about 2 (for details, see **Paper V**). Thus, it is likely that that fraction consists mostly of C4–C5 hydrocarbons and some additional BTXS.

At 800°C, the unidentified fraction at the industrial size was about 26%C, with an estimated H/C ratio of 1.2, which is in line with the under-estimated level of benzene and the small fraction of C4–C5 C4–C5 hydrocarbons. In the laboratory test at 800°C, the carbon content in

C4–C5 hydrocarbons was only 2%C and total BTXS measured was 11% points higher than the measured in the industrial site. However, this only explains about 13%C of the unidentified carbon, leaving more of 10%C still unknown.

From the measurements obtained at the laboratory and industrial scales, there were no clear indications of additional missing hydrocarbons. There was, however, a clear increase in the levels of PAHs at higher severities. The pronounced increases in the PAHs, in terms of both molecular weight and total yield, under more-severe conditions are well-known for polyolefins, and even more so for PVC, for which a tendency towards soot is expected due to the unfavourable H/C ratio of the polymer. Knowing the mechanism of thermal PVC decomposition, it is reasonable to suspect that a small amount of the carbon in the fuel will be found as soot, here defined as PAHs with >20 carbon atoms.

To understand further the formation of PAHs, a GC-MS analysis of the aromatics, i.e., the SPA sample, was performed for the test with temperature of 800°C. Many PAHs were detected. The polycyclic structures with three or more rings, from fluorene C₁₃H₁₀ to pentacene C₂₂H₁₄, accounted for about 3% of the carbon in the fuel, i.e. half if the total PAHs measured. This indicates the possibility of there being a few %C in higher growth of the PAHs.

The GC-MS analysis also provided information concerning heteroatoms. Cable plastic contains some oxygen, very small amounts of N and S, and a considerable amount of Cl in the feedstock. Even though the amount of oxygen in the feedstock was small, about 6% and 4% of the oxygen was found in the aromatic fractions, while we observed the same trend of decrease with temperature. All of the S in the fuel was in the form of H₂S.

Some nitrogenated and chlorinated compounds were detected in the GC-MS at 800°C. For N, the calibrated compounds (aniline, benzonitrile and p-toluidine) were not detected, although some N-containing compounds were detected in the GC-MS. Overall, about 15% of the feedstock N was found in the aromatics (mostly in forms of 9,10-dihydro-acridine, C₁₃H₁₁N, and nonanamide, C₉H₁₉NO).

The GC-MS also detected small amounts of chlorinated hydrocarbons. About 13 ppm of Cl were detected in the aromatics fraction at 800°C in the forms of two different compounds that contained 20 and 21 carbons, respectively. However, these accounted for less than 0.1% of the Cl in the feedstock.

Textiles (TXT)

Textile residues were tested at two temperatures, 730°C and 790°C. The screw feeder was used, with feeding rates of about 150 kg_{daf}/h and 120 kg_{daf}/h at the low and high temperatures, respectively. The steam flows were 160 kg/h at 730°C and 140 kg/h at 790°C and silica sand was used as the bed material. These results are taken from **Paper VI**.

The methods used for the assaying the TXT were **micro-CG** for permanent gases, **double SPA** for the aromatics, and **HTR** for the total carbon converted into gas. For these experiments, the main limitation was the lack of analysis of C₄–C₅ linear hydrocarbons, which should not be significant given the low levels of aliphatic plastics in TXT.

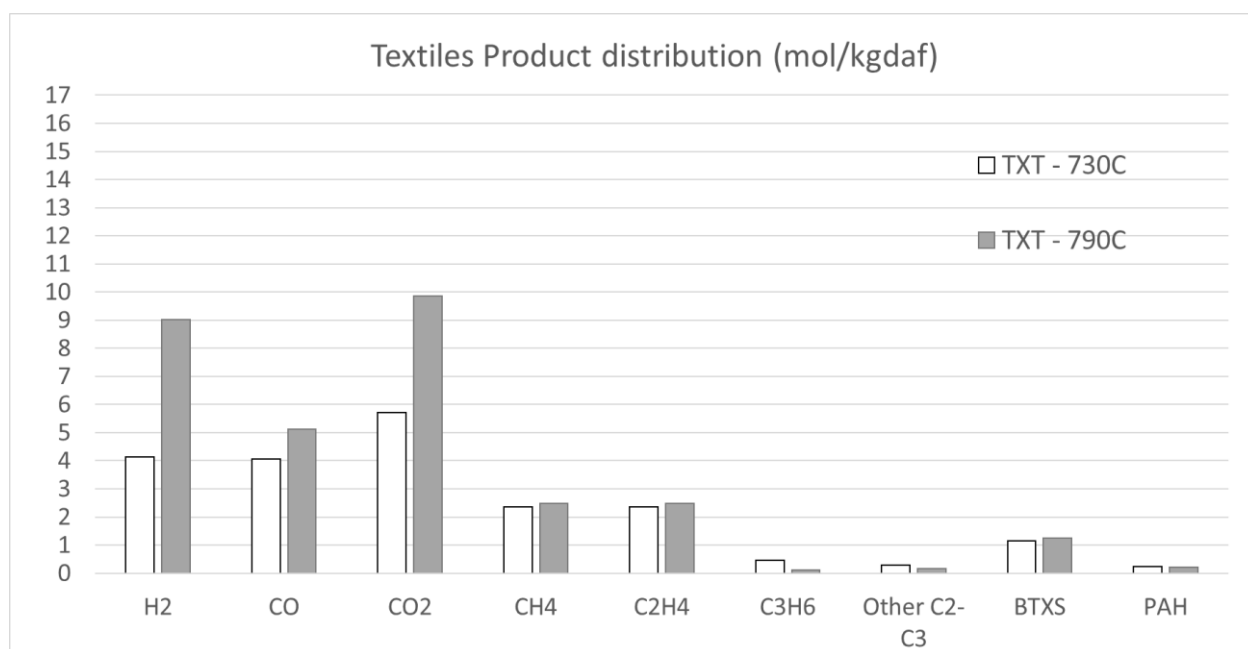


Figure 15. TXT product distribution from steam cracking (mol/kg_{daf})

Figure 15 shows the gas distributions from TXT steam cracking (in mol/kg_{daf}) at the two temperatures. The most-abundant gas products were H₂, CO and CO₂, for which the yields increased with increasing temperature. The H₂ yields more than double between 730°C and 790°C. The CH₄, C₂H₄ and BTXS yields remained similar, with only a small increase noted with increase in temperature. In contrast, the yields of propylene and other C₂-C₃ species decreased, while the PAH yield remained almost constant.

While the molar distribution did not show significant changes (other than for CO₂), the carbon balance showed a higher level of variation due to the relatively low carbon content of the fuel (see Figure 16).

As observed, the carbon contents of the CO_x increased with temperature, from 19%C to 29%C, while methane was 5%C for both conditions. The concentrations of C₂-C₃ hydrocarbons decreased with temperature, from 10%C to approximately 7%C. In contrast, the concentrations of BTXS increased slightly with temperature, from 14%C to 15%C, while the PAH concentrations were about 4%C in both cases.

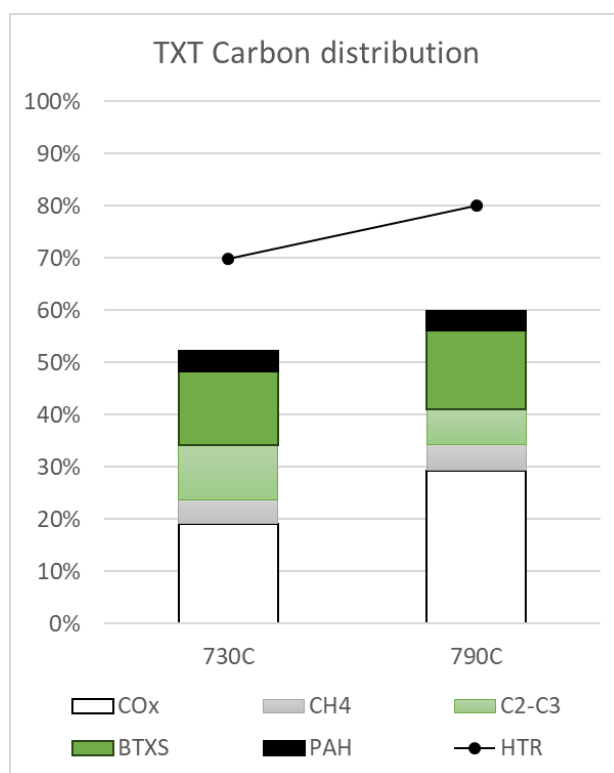


Figure 16. Carbon distribution from steam cracking of TXT

Overall, the total carbon measured in the gas with the HTR varied substantially: from about 70%C for 730°C, to around 80%C for 790°C. Of the gas compounds, 52%C and 60%C were measured, while the unidentified for TXT was significant, accounting for 18%C and 20%C at 730°C and 790°C, respectively. As stated above, the C4–C5 hydrocarbons were not measured. However, given the low level of formation of C2–C3, only a few percentage points could be expected. To gain a better understanding of the unidentified fraction, we can examine the GC-MS analysis of the aromatic fraction samples (SPA).

In the GC-MS analysis of the aromatics, many PAHs were detected. The polycyclic structures with three or more rings, from fluorene $C_{13}H_{10}$ to pentacene $C_{22}H_{14}$, accounted for about 2% of the carbon in the fuel. Only a few other aromatic compounds $>C_{18}$ were found, and the highest was $C_{20}H_{10}$. This indicates that not a significant PAHs growth can be expected.

Therefore, other unidentified hydrocarbons products are likely. Given the high content of nitrogen in the TXT (about 4%_{daf}), the production of N-containing compounds was further studied.

The GC-MS analysis detected many aromatics that contained N. The calibrated compounds (aniline, benzonitrile and p-toluidine) were detected, and other N-containing compounds were detected in the GC-MS. About 6% and 5% of the N content of the fuel was found in the aromatics at the two temperatures tested, which were mostly (>60%) the calibrated compounds (aniline, benzonitrile and p-toluidine).

The detected and measured N-aromatics accounted for about 2%C. TXT contain rubbers and polyamides, albeit mostly PA, which can decompose into nitriles at the temperature tested. Thus, it is possible that other N-containing compounds were present. If the remaining N was found as HCN, it would correspond to more than 5%C. Similarly, if it was found as C_2H_3N it would correspond to 11%C, or 16%C if it was found as C_3H_5N . Therefore, significant amounts of carbon can be present in such N-compounds. These N-containing compounds partially explain the unidentified species, although 5–10%C remains unidentified. Another possible explanation for the unidentified fraction is the feeding irregularities experienced during these experiments, which will be further discussed in the next section.

Regarding other heteroatoms, TXT also contain some S and Cl, very low amounts of fluorine (F), as well as a significant amounts of N and oxygen in the feedstock.

Again, the oxygen was found mostly as CO, CO₂, although a significant amount was present in the aromatics fraction, about 5% and 3% of the feedstock oxygen, at 730°C and 790°C, respectively. For N, the calibrated compounds (aniline, benzonitrile and p-toluidine) were detected, although some additional N-containing compounds were detected in the GC-MS.

Some S- and F-containing compounds were detected in the GC-MS. While most of the S ended up as H₂S, a small fraction was found in the aromatics, accounting for 1% of S at 730°C and 10% at 790°C. The GC-MS also detected one F-containing hydrocarbon at 790°C, accounting for about 30% of the F in the feedstock, and none at 735°C. Similarly, one chlorinated hydrocarbon was detected, but only at 790°C, and it accounted for less than 0.1% of the Cl in the feedstock.

Cardboard recycling (CBR)

The CBR residues were tested at two temperatures, 740°C and 805°C. The extruder feeder was used, at feed rates of about 35 kg_{daf}/h and 40 kg_{daf}/h at the low and high temperatures, respectively. The steam flow was 150 kg/h for both cases, and silica sand was used as the bed material. These results are taken from **Paper VI**.

The methods used for these tests were **micro-CG**, **double SPA** and **HTR** for the total carbon converted. For these experiments, the analysis of C4–C5 linear hydrocarbons was performed using GC-VUV, given the high aliphatic content.

Figure 17 shows the gas distributions following CBR steam cracking (in mol/kg_{daf}) at 740°C and 805°C. The most-abundant gas products were H₂, CO, CO₂, CH₄ and ethylene, for which the yields increased with increasing temperature. The yields of H₂ increased significantly when the reactor temperature increased from 740°C to 805°C, and the yields of CH₄ increased by 20%. The CO, CO₂ and C₂H₄ yields remained similar, with only a small increase noted with increase in temperature. In contrast, the yields of other C2–C3 and C4–C5 species decreased.

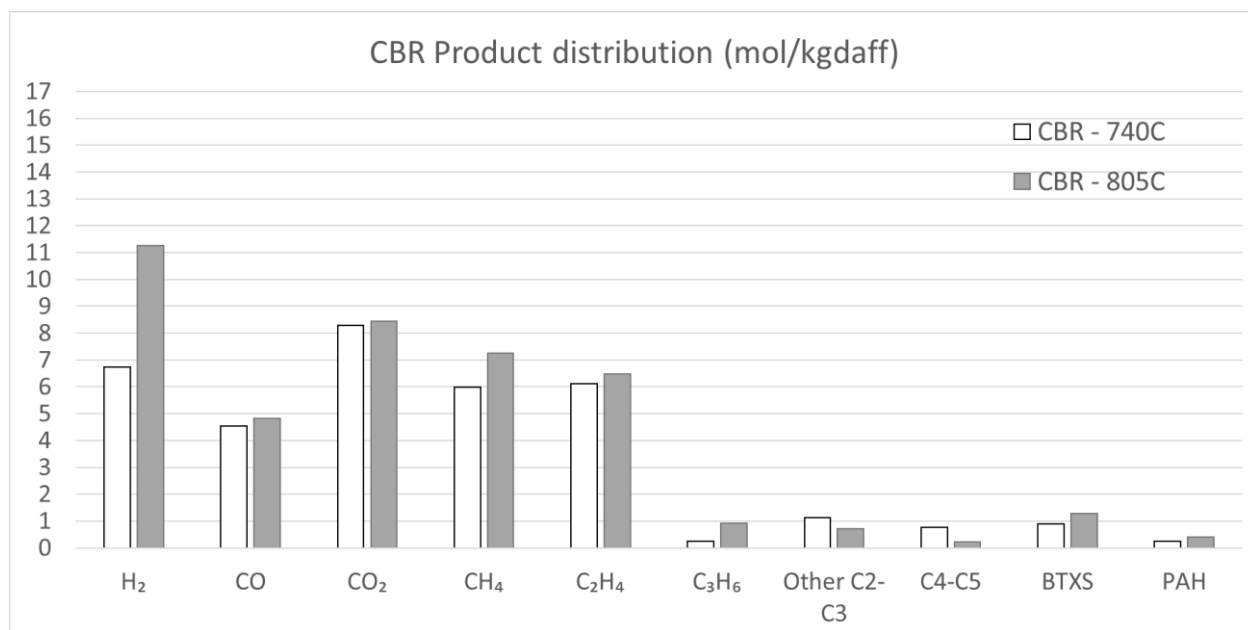


Figure 17. CBR product distribution from steam cracking (mol/kg_{daf})

Overall, as already observed for other wastes, lower concentrations of aromatic compounds were seen at 740°C than at 805°C, (1.15 mol/kg_{daf} vs. 1.7 mol/kg_{daf}). The main product in the aromatics fraction was BTXS, the level of which increased with temperature. There was also a clear increase in the levels of PAHs with increasing temperature.

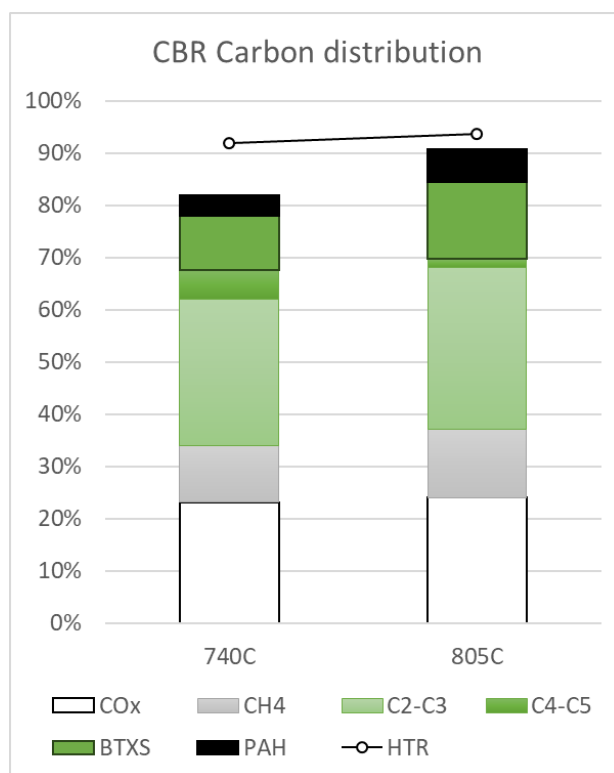


Figure 18. Carbon distribution from steam cracking of CBR

The carbon distributions of the products leaving the cracker are shown in Figure 18, where 100% corresponds to the total carbon in the CBR. The products are divided into the same categories as before, but the C₄–C₅ hydrocarbons was added, given the addition of the GC-

VUV measurement. Also, it must be noted that the SPA method used was the **double SPA** technique.

The percentages of carbon in the form of CO_x were 23%C at 740°C and 24%C at 805°C. CBR produced significant amounts of carbon aliphatic form, CH₄ was 11%C and 13%C, and the C₂-C₃ fraction, 28%C and 31%C at the low and high temperatures studied. In addition, 6%C is found in C₄-C₅ hydrocarbons at 740°C, and only 1.5%C, at 805°C (consisting of mostly C₄ hydrocarbons in both cases). For the aromatic fraction, CBR yielded about 10%C and 15%C in BTXS, and an additional 4%C and 6%C in PAH, at the low and high temperatures, respectively.

Compared to the previous waste, less amount of carbon is unidentified. The unidentified carbon is 10% at 740C and only 3%C at 805°C. It can be expected that the unidentified fraction consists mainly of unmeasured hydrocarbon species and/or soot particles. Given that most linear hydrocarbons were measured, it is unlikely to be that. The unidentified compounds can be PAH or soot with C>18.

Correlation of polyolefins to C2–C3 carbon species

Given the results obtained for different waste mixes, a more-systemic analysis was performed to identify any trends or relationships between the production during steam cracking of the wanted HVCs and the material contents of the waste or the carbon bonds therein.

Figure 20 shows the correlations between the polyolefin contents and the production levels of C2 and C3 hydrocarbons, in carbon percentage. The results for the five mixed wastes at a temperature of around 800°C is represented with the blue line, and at around 735°C with orange line.

There is a linear and positive correlation between the content of olefinic polymers in the feedstock and the production of aliphatic hydrocarbons with two and three carbons. This follows the same order of higher content of polyolefins, higher carbon fraction in C2–C3 hydrocarbons at 730°C (i.e., CP > CBR > TXT). However, at 800°C, there are minor discrepancies between CBR, TOP and ASR. For ASR, this may be because the main polyolefins are PP and polyisoprene (19% and 13%), which have lower yields than PE. In contrast, for CBR, much more is produced at 800°C, perhaps due to the different feeding systems used. In addition, TOP deviates to some extent; nevertheless, the PO content is only a fictitious estimate.

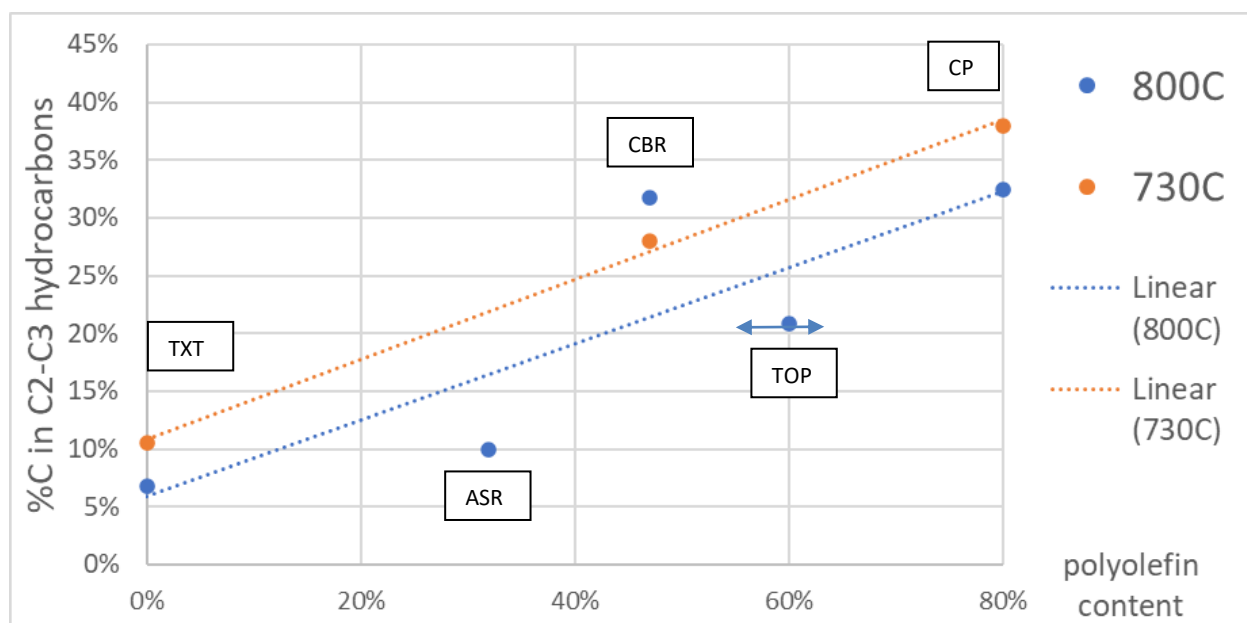


Figure 19. Carbon content (%C) in C2–C3 hydrocarbons versus polyolefin content in the feedstock at two different temperatures.

We can also study the correlation between each type of bond and the product's distribution. The left-hand panel in Figure 20 shows the %C in CO_x versus the CO bonds content. The right-hand panel shows the %C in the C2–C3 hydrocarbons and CH₄ versus the C-AL bonds content.

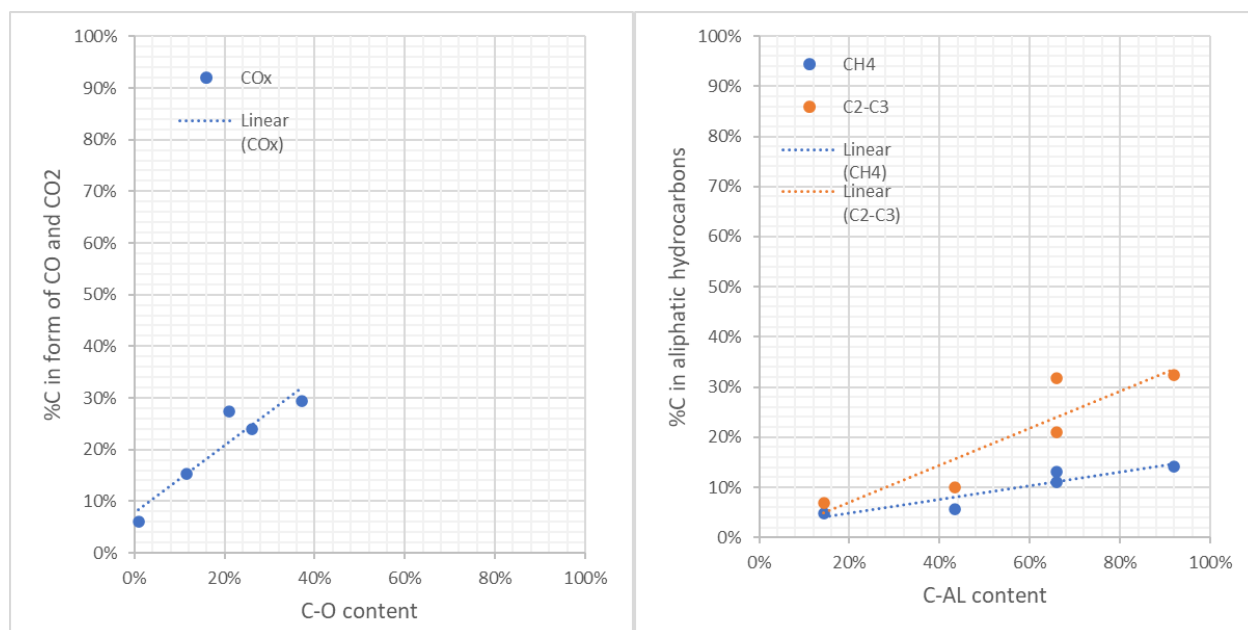


Figure 20. Carbon products at 800°C. Left panel: %C in CO_x versus C-O bonds content. Right panel: %C in CH₄ and C2–C3 species versus C-AL bonds content in the feedstock.

CO_x is positively and apparently linearly correlated with the C-O bonds. Similarly, both the C2–C3 hydrocarbons and CH₄ show a positive correlation with the C-AL bonds. However, in many of the experiments, other linear hydrocarbons were not measured. Therefore, further analyses are needed with the new measurement techniques to obtain a clearer picture.

Figure 22 shows that there is no apparent correlation of the aromatic content with the C-AR. However, the precise total aromatics content is unknown for TOP and ASR (a range is shown in the graph). Overall, it seems that the aromatics production is around 20%C for all cases, independent of the aromatics content. This may be because the formation of aromatics depends on both the aromatics content and the cyclisation of linear hydrocarbons.

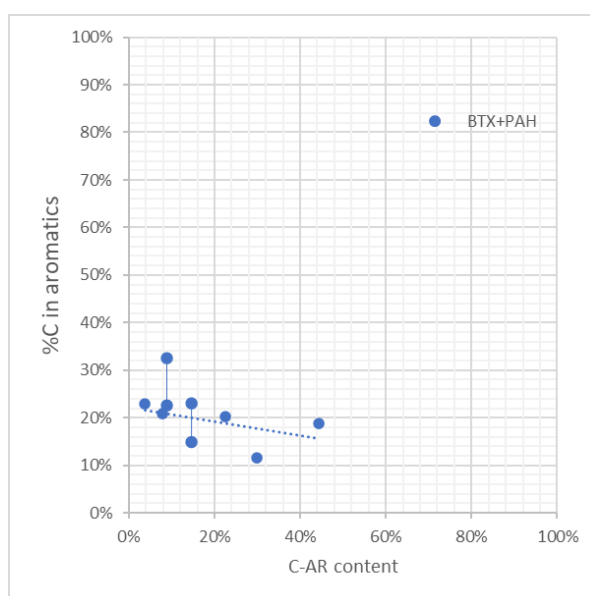


Figure 21. %C in Aromatic at 800°C versus C-AR bonds content in the feedstock.

Discussion measurements

Improvements have been made to the measurement techniques over the years, allowing the identification of more products. The TOP experiments show that some aliphatic hydrocarbons are not identified and that the levels of some mono-aromatics are under-estimated, leaving an unidentified fraction of around 30%C. In addition, the carbon measured in the gas with the HTR corroborate the presence of unidentified carbon-containing products in gas form. The ASR tests show that 7%–9% of the carbon is unidentified, and this may represent unmeasured mono-aromatics. Thus, developments were made to characterise fully the product distribution and including a comprehensive analysis of aliphatic hydrocarbon and aromatics.

Given the material composition of CP, it is likely to produce both aliphatic hydrocarbons with four or five carbons and more aromatics, due to its PVC content. Thus, adjustments were made to the measurement method to include these products. While these measurements were not ready to be tested in the industrial plant, the experiments to assess those compounds were repeated in the laboratory. Changes were made to the SPA method to capture all the aromatics using a technique named here as *double SPA*. In addition, the C4–C5 hydrocarbons were included in the micro-GC employed. As shown, these improvements give a complete picture of the product distribution at 730°C. However, at 800°C, about 10%C was still unidentified.

With the increase in reaction temperature, secondary reactions are promoted, promoting the growth of PAHs. In addition, with a higher severity, the dehydrochlorination process may be incomplete, so some of the Cl in the PVC may be present as chlorinated compounds. The CP contains mainly PE, but the presence of PVC leads to PAH formation, which enhances the formation of soot. Thus, a few percentage points of carbon can be expected in the form of soot.

The developments involving the SPA and C4–C5 measurements were also included in the industrial experiments for TXT and CBR, contributing to 10%–20% of the carbon in the additional products measured. Both techniques contributed to the understanding of the product distribution of CBR, while only mono-aromatics were added to the TXT, since linear C4–C5 hydrocarbons were not detected.

The unidentified fraction in the CBR is relatively small, less than 10%C at 740°C and only 3%C at 800°C. At 800°C, we see the same increase in PAH as in CP, so it could be soot. Soot formation depends on the residence time and the fuel. For instance, other authors have described soot as having 1%C during PE gasification under similar conditions[47]. For PA and PUR, soot has been reported as having around 3–4%C[59]. For mixed municipal solid waste, the soot has 1–8%C, at 805°C for a gas residence time of 3 s. Similarly, for mixed polyolefin waste, the soot is 0.8%C[53], for a gas residence time of 5–6 s. Both ASR and TXT have high contents of PA and PUR, which also generate more soot. In particular, TXT has a high content of PAHs, so a few percentage points of carbon may be in the form of soot. However, the total unidentified fraction is around 20%C, which means that there must be another explanation. One possible explanation is hydrocarbons that contain heteroatoms.

All the plastic wastes studied have a significant quantity of heteroatoms, which can lead to some non-identified hydrocarbons containing these atoms. As described in the *Background* section, each polymer has a distinct decomposition pathway, in particular, those with heteroatoms such as PVC, PU and PA.

As we have seen, the material content estimate for ASR shows about 24%wt of PU/PA and about 2% of PVC. While no Cl-aromatics were found, a few nitrogenated compounds were detected. There are significant amounts of polyurethanes in ASR, and their decomposition can lead to generation of the radicals R-CN and R-NH₂, which are both aromatic and linear hydrocarbons. Similarly, the formation of aliphatic nitriles in TXT steam cracking are highly possible, since they are part of the decomposition of PA [73,74].

While the improvements in the measurements of aliphatic and mono-aromatics are significant, further research is needed on the N-containing compounds and other heteroatoms in different waste streams.

A significant part of the products was not in gas form, i.e., not measured in the HTR. These can be non-fully devolatilised feedstock that exit the steam cracker with the bed material or dust/particle borne by the gas without being sampled.

The formation of char and the non-fully devolatilised fuel are closely related, since char is the material that remains after the pyrolysis/devolatilisation process. Ideally, the char should consist of only carbon (or a very low H/C ratio) and ash, or both ash and fixed carbon (FC). The percentages of FC obtained from the proximate analysis obtained via thermogravimetric analysis (TGA) are: 12%C for ASR; 4%C for CP; 19%C for TXT; and 1%C for CBR. The main observation from this analysis is that there is a part of the fuel that does not undergo full conversion.

To study these effects further, the ASR devolatilisation was tested in the laboratory reactor at 800°C (**Paper IV**). The solid/ non-fully devolatilised feedstock left in the bed material accounted for 20% of the carbon in the feedstock. The first observation is that the FC from ASR was 12%C, is much lower than the measured in the laboratory, 20%C, proving that there is still non-fully devolatilised feedstock. In comparison, 30%C was not measured in the gas during the industrial test.

This 10-percentage points difference carbon may be linked to the solid particles >2 microns formed (for example soot), different devolatilisation from the two reactors or feeding variations. In the laboratory reactor, only one pellet was fed at a time, whereas in the big-scale reactor, other factors could play a role. For instance, de-gassing 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.

The various sources of feeding variations include: a small variation in the feeding rate; variations in the fuel composition; the fuel not reaching the reactor temperature due to being segregated together near the feeding point; and dust being carried by the gases. Such as dust pass through the raw gas line without being sampled and measured with the HTR, either do to being bigger than the filter mesh (>2 microns) or due to its flight pattern.

The effects on the conversion of variations in the feeding rate should be minimised by the duration of the measurement, which is 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 the 148 kg/h, which translates to a $\pm 3\%$ variation.

Variations in fuel composition can also lead to a defective carbon balance. Thus, the TXT fraction was analysed in detail to detect possible variations in the elemental and polymer compositions and in the proximate analysis. Four different batches of TXT were tested in the elemental and proximate analyses, and the deviation was always $<1\%$. The material composition was also analysed, resulting in a deviation of $\pm 2\%$ in the material content. Thus, the fuel heterogeneity should 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 borne by the gases. Pellets may aggregate together near the feeding point, which may cause a local temperature to drop due to the heat required for devolatilisation and melting, and this may be sufficient to decrease the devolatilisation rate. This phenomenon was observed during TXT feeding, whereby a significant amount of fluffy material became stuck in the feeding shaft. Dusty and/or light materials can disperse 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 the ASR.

Discussion: Hydrocarbon recovery

As mentioned in the *Background* section and in *Part I*, the petrochemical industry is based on HVCs, i.e., ethylene, propylene and BTXS. However, the product distribution from the steam cracking of wastes not only includes the wanted HVCs, but also other compounds. On the one hand, the CO, CO₂ and aromatic compounds production during waste steam cracking is greater than from naphtha steam cracking, and also has many more aromatic compounds. On the other hand, we have detected the presence of heteroatoms in the products.

Table 8 summarises all the results from the steam cracking of mixed wastes in %, dry ash free basis, and includes the product portfolio of naphtha steam cracking as a reference. Steam cracking of naphtha produces about 16% of syngas, where only 1% is H₂ and CO_x and 15% is CH₄. The main products are ethylene (25t), propylene (15%), and BTXS (12%). In addition, 5% is found as butadiene and 16% as other linear hydrocarbons.

If we compare the desired hydrocarbons produced from the steam cracking of mixed waste products to the products of naphtha steam cracking, it is clear that the yields of linear hydrocarbons are always lower. The ethylene and propylene produced from waste ranges from 7% to 31%, while the corresponding value for naphtha is about 40%. The closest to this is CP, which generates 31% of these two compounds, followed by CBR with about 20%, since they contain more aliphatic content in the waste. In contrast, ASR and TXT produce low levels of ethylene and propylene, at 7–8%. The BTXS produced are more or less similar for all the wastes, with the exception of ASR and TOP, though the measurement

Table 8. Summary of the results from steam cracking of different wastes (in %daf) at different temperatures.

%daf	Naphtha Steam cracking	TOP - 770C	TOP - 825C	ASR - 790C	ASR - 825C	CP - 730C	CP - 800C	TXT - 730C	TXT - 800C	CBR - 740C	CBR- 805C
H₂,CO, CO₂	1%	42%	53%	65%	84%	12%	16%	37%	60%	50%	53%
Methane	15%	12%	13%	5%	6%	10%	14%	4%	4%	10%	12%
Ethylene	25%	12%	14%	6%	6%	21%	24%	6%	7%	17%	18%
Propylene	16%	5%	3%	2%	1%	10%	3%	2%	1%	1%	4%
Butadiene	5%	n.a.	n.a.	n.a.	n.a.	6%	2%	n.a.	n.a.	4%	1%
Other C2-C5 hydrocarbons	16%	3%	2%	1%	1%	10%	3%	4%	3%	4%	2%
BTXS	12%	14%	12%	4%	5%	14%	14%	9%	10%	7%	10%
Other aromatics	n.a.	5%	7%	4%	4%	5%	9%	3%	3%	3%	5%

n.a.: not available

Another difference between the steam and cracking processes is the amount of CO and CO₂ produced, which is always significantly higher for steam cracking. On the one hand, the majority of the heteroatoms in the waste are oxygen (O). At the studied temperatures, the O is mainly present as CO and CO₂ in the lighter fraction of the gas. As a consequence, a significant amount of carbon is found in the syngas. Thus, we need to find ways to recover as much

carbon as possible, and separate the syngas from the wanted HVCs. On the hand, CH₄ production is lower for waste steam cracking (at the studied temperatures).

The syngas is potentially usable in different synthesis processes if it has a suitable H₂/CO ratio (in the range of 2–4). However, the CO₂ and CH₄ will need to be converted into syngas in order to be recovered. For instance, to produce methanol, the synthesis requires an H₂/CO ratio of 2 or 3, depending on the process. Given that the total H/C ratio is around 1 for both ASR and TXT, there is a deficit of hydrogen for the production of methanol. In contrast, for CP, this gas fraction has a high H/C ratio, although this is mainly due to the high CH₄ content, which will need to be transformed into syngas.

While other heteroatoms do not contain a significant amount of carbon (in general, other than TXT), it may be difficult to recover the wanted hydrocarbons. For instance, the presence of H₂S and/or HCl requires a cleaning system to recover the ethylene and propylene, as well as the syngas.

The presence of O in the aromatics fraction is relevant for its recovery. Oxygen in the aromatic compounds makes up less than 1.0% for the ASR and TOP, but around 5% for the CP and TXT. All of the wastes showed the same trend of decreasing O levels in the aromatics when the temperature was increased. Moreover, none of the aromatics is within the boiling point range for benzene and styrene.

The presence of other heteroatoms in the aromatics fraction is also relevant for its recovery. The chlorinated compounds were examined in detail for ASR, CP and TXT by GC-MS analysis, revealing that no chlorinated aromatics were present or that there was less than 0.1% of Cl in the fuel. In addition, when Cl was found the aromatic hydrocarbons had a carbon number >19.

However, N-containing aromatics were found in the TXT and ASR fractions, comprising about 5% of the N in the fuel. The main compounds detected were aniline, benzonitrile and p-tolunitrile. Given the presence of PA in the waste, it seems likely that acetonitrile and acrylonitrile were also present in the permanent gas, although they were not measured. Both compounds have boiling points similar to that of benzene, which may hinder the separation and recovery of benzene. Therefore, the N-containing compounds need to be studied in greater detail in the future.

REFLECTIONS

Reflection carbon circularity

Carbon materials, such as paper, wood, plastics and textiles, play important roles in our everyday lives, encompassing clothes and packaging to infrastructure. The use of those materials follows a linear pathway, with high levels of resource consumption, emissions, and waste generation. This work estimated that C-Materials require more than 1000 Mt of carbon in resources, are responsible for emissions of up to 3 GtCO₂ and generate almost 500 MtC in waste.

Many of C-Materials are essential and demand for them is projected to grow even further. C-Materials recycling is an alternative way to reduce resource consumption, emissions and waste. However, current recycling systems have serious limitations, in that they can only process clean streams and generally produce products of lower quality.

Thermochemical recycling is a way to recover carbon from waste, although current research focuses mainly on clean plastics, such as polyolefins, and studies of other waste mixtures, for which other recycling techniques fall short, are generally lacking. To achieve carbon circularity, it needs to be established that there is sufficient carbon in the waste to close the loop, and it needs to be known which types of waste can or need to be recycled.

This work provides an estimate of how much carbon is available and what types of C-Materials waste exist. It shows that there is enough carbon in the waste (>300 MtC) to produce the desired HVCs for synthetic C-Materials. This waste consists of approximately 40%C natural C-Materials and 60%C synthetic C-Materials, on a carbon basis. It also shows that C-Materials that readily decompose into the desired HVCs, i.e., polyolefins, only account for ≤25% of the carbon.

The available waste is likely to be a highly heterogeneous mixture of synthetic and natural C-Materials, so its thermal decomposition is complex and depends on the feedstock. Therefore, studies of mixed streams are needed to define the products of gasification. Five distinct mixed wastes were studied to assess the possibilities and limitations associated with thermochemical recycling.

Thermochemical recycling of mixed waste

Thermal decomposition depends on the feedstock that is employed. Here, five distinct wastes were studied, with different contents of natural and synthetic materials, as well as different contents of polyolefins. From the synthetic C-materials, CP had the highest content of polyolefins, followed by CBR and ASR, while TXT had no polyolefins. In addition, a purely natural C-Materials with high aliphatic content was included, which corresponded to about 60% polyolefins content. The results show that a higher polyolefin content in the waste produces higher shares of C₂–C₃ hydrocarbons.

The waste also contained polymers with high contents of aromatics, such as PET, PS and PU, although no clear relationship was found between the aromatics content of the polymers and the aromatics share in the products.

The mixed waste was useful for an initial exploration of the fate of the heteroatoms. CP had about 14% PVC, whereas the Cl content of the aromatics fraction was negligible at 800°C. In addition, ASR and TXT also contained Cl, and the results showed that the Cl content in the aromatics fraction could be avoided by increasing the temperature. Increasing the temperature is also shown to reduce the O and N concentrations in the aromatics fraction.

While increasing the temperature reduced the levels of heteroatoms in the aromatics fraction, it significantly increased the amount of CO, CO₂ and CH₄ produced. This left a substantial amount of carbon to be recovered. Overall, the results show that thermochemical recycling of mixed wastes can lead to the direct recovery of 20–50% C in the forms of ethylene, propylene and BTX. Nevertheless, to achieve 100% recovery of the carbon, we also need to recover the non-fully devolatilised feedstock and carbon products containing heteroatoms, together with the carbon in the forms of CO, CO₂, CH₄ and other compounds.

Another finding that emerges from the mixed waste steam cracking test is the need for measurements of S, Cl and, most importantly, N. While these heteroatoms do not represent a significant amount of the carbon, it may be difficult to recover the wanted hydrocarbons. For instance, the presence of H₂S and/or HCl requires a cleaning system to recover ethylene and propylene, as well as the syngas. Many of the N-containing aromatics were found in the TXT and ASR fractions, being mainly aniline, benzonitrile and p-tolunitrile. Given the presence of PA in the waste, it is likely that acetonitrile and acrylonitrile were also present in the permanent gas, but they were not measured. These two compounds have boiling points similar to that of benzene, which may hinder its recovery.

Perspective carbon recovery of mixed waste

The wastes studied in this work advance our understanding of steam cracking of mixed wastes with different characteristics. However, we must ask: *How representative of the available waste are these mixed wastes?*

Figure 7 shows the carbon distribution in the available waste (estimated). If we start with textiles, we can see that they account for about 10% of the carbon available. While CP and ASR are waste streams with relatively small flows, they represent waste from transport, consumer products and the electrical sector, which account for more than 10%C of the waste. CBR is a good representative of packaging waste, which contains both paper and plastics. While it is difficult to quantify how much of the waste will be in the form of such a mix, we know that more than 40%C of the available waste is packaging (both paper and plastics together). Thus, it represents a significant amount of the waste.

Although TOP does not represent a specific type of waste, it is a good example of how a left-over flow from the production of paper products, and not waste per se, could be used to close the loop of carbon material. The missing component in available waste is wood; however, extensive research has been done on the steam cracking of biomass (often called *gasification*). As described in the *Background* section, the main product is syngas, together with a very small amount of BTXS.

If we place in the global perspective the results of the steam cracking of the waste, we get a clearer idea of what is needed to achieve carbon circularity. *Figure 22* summarises the recovery of the carbon in the mixed waste estimated as the HVCs needed in the chemical industry for synthetic C-Materials. The results are taken from the steam cracking of waste at 800°C, which produces some products that are the same as the HVCs, while other products require further transformation steps.

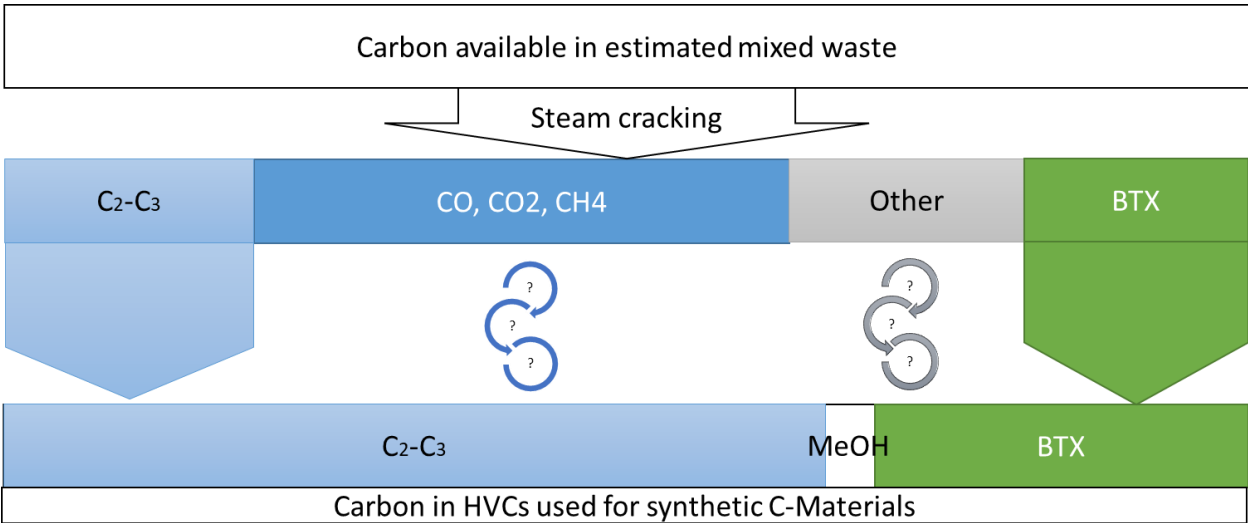


Figure 22. Carbon recovery from the mixed waste into HVCs via steam cracking.

Ethylene and propylene can, in principle, be used directly in the petrochemical industry. Other linear hydrocarbons can also be used, although this entails further treatment. This treatment is similar to what is already performed after the steam cracking of naphtha, so it is possible to integrate the process with refineries/fractionation plants. As stated above, a significant share of the carbon is in the form of syngas. This fraction can be synthesised, for example, into methanol and followed by methanol to olefins process. Similarly, the non-fully devolatilised feedstock and the PAHs can be combusted, and the energy produced can be used in the gasification process with subsequent recovery of the CO₂. However, the viability of this process needs to be confirmed in future studies.

Conclusions

Carbon-containing materials, such as paper, wood, plastics and textiles, produce GHG emissions along their supply chains. From its extraction and manufacture and, unlike other materials, also at the end-of-life stage, these materials release their embedded carbon into the ecosphere. Recycling materials using current methods cannot achieve a circular economy because the current system entails material degradation and losses. As an alternative, this thesis shows that emphasising carbon recovery, instead of material recovery, provides a new and valuable perspective on carbon-containing waste flows.

The material flow analysis of the current carbon material system illustrates that the system losses are greater than the produced carbon material, and are equivalent to about 6% of the GHG emissions. It also shows that the feedstock demand for production can be covered purely by the carbon in the waste. By using this carbon, we can de-couple fossil resource extraction and reduce GHG emissions by half.

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

The thermochemical recycling of five different mixed wastes was tested in an industrial scale reactor, to understand the product distribution. The experimental results show that the conversion yields a mixture of gases and aromatic compounds. The carbon distribution consists of 5%–40%C syngas, 5–40%C ethylene and propylene, about 20%C BTX, and 15–50%C other compounds. While some of these can be used directly, if their concentrations justify separation (C2–C3 hydrocarbons and BTX), the remaining compounds require further recovery and processing.

Another finding is that a higher conversion temperature helps to limit the levels of heteroatoms in the hydrocarbons. For instance, the Cl content of the aromatics fraction can be avoided by increasing the temperature to 800°C. Increasing the temperature also reduces the O and N contents of the aromatics fraction. However, there is still a need to develop further our understanding of the distributions of nitrogenated compounds.

Overall, the experimental investigation demonstrates that thermochemical recycling has the potential to promote a circular economy and to reduce emissions. Nevertheless, further efforts are required to tackle the different challenges in order to establish thermochemical conversion as a viable recycling method for mixed wastes.

Recommendation for future work

As presented in this thesis, recovering carbon from mixed waste is essential to achieving a circular economy and reducing emissions. Global application of feedstock recycling technologies has the potential to reduce carbon emissions and resource usage. In addition, the mixed waste tests show that not only HVCs will be produced, but also other products that require a transformation step. Thus, further work is needed to identify deployment strategies and to explore in depth the integrated technologies, as well as the energy and economic implications of deployment.

The experimental investigation also highlights areas that require additional efforts to tackle the different challenges facing the application of thermochemical conversion as a viable recycling method for mixed wastes. Investigations are needed to elucidate mixed waste conversion, including heteroatoms. Further improvements are recommended for the sampling and analysis, so as to close the carbon balance, with a more-detailed study of the effects of heteroatoms as well as soot/particles in the gas.

The results in this thesis point out that, aside from HVCs, we need to make use of syngas, PAHs, and other fractions. 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 HVCs and methanol. Not only that but also the possible effects of contaminants on the recovery rates of HVCs and other gases deserve attention. The present work has focused mostly on heteroatoms, highlighting some research gaps, but there are other possible contaminants. Waste often contains ash, such as metals, and the fate of those ashes in the products warrants investigation.

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