The Renewable Future of Materials

How to produce our everyday products once we phased out fossil oil and gas

HARRIËTTE BOS, DAAN VAN ES, PAULIEN HARMSEN

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Preface

Materials are all around us. Just like food they are an indispensable part of our everyday life. We wear them, sit on them, drive in them and live in them. What not everybody may realise, is that part of the materials we have become so accustomed to, are made from fossil resources, mostly from the oil that is also used to produce petrol and diesel.

Therefore, the phasing-out of fossil feedstocks, something that has become a very pressing issue due to climate change, not only means finding new energy solutions. Phasing out fossil feedstock also means we need to find other ways to make a significant part of our materials, maybe develop new materials, and also to be more caring and aware in our attitude towards the materials we use every day. Without the abundant availability of the cheap and versatile feedstock, fossil oil, we are going to face a tough future to clothe ourselves and furnish our homes.

In our modern society, we use different types of materials: glass, cement, bricks, metals, etcetera. But in this booklet we focus on a specific type of materials, the materials that are made from carbon. You find these materials in all textiles, in packaging, in building and interior materials, in cars, in sports-equipment and much more. Up till now, fossil feedstocks and biomass are the main suppliers of these materials. Presently much used biomass-based materials are mostly cotton in textiles, wood in paper and board, and wood in building and interior applications. Fossil feedstock-based materials are for instance polyester (in textiles and bottles), plastics in all kinds of products, paints and glues, etcetera. With the phasing out of fossil feedstocks we need to find a large renewable source for these carbon-based materials, and we cannot put the full burden on biomass.

Several professionals realised recently that there are three, and only three options to source fossil free carbon-based materials: using biomass, applying CO_2 capture and utilisation technologies, and using recycled materials. In our discussions with colleagues and other stakeholder we realised that it is difficult to grasp the differences and similarities between these three feedstock options for the production of materials. However, when seen from a chemical and polymer science angle, there is a logical structure underlying these three production routes for carbon-based materials.

It is therefore that we wrote this booklet. In the first two chapters we highlight the role of carbon in our everyday materials, and we present a framework of the basic similarities between all carbon-based materials. Building on this framework, we then describe how the three different feedstock routes can contribute to our future materials supply: Biomass in Chapter 3, CO_2 technologies in Chapter 4 and recycling in Chapter 5. Chapter

6 is dedicated to the complexities in the production chains for materials, and the roles of specific stakeholders towards realising the materials transition.

We hope that you will enjoy reading this booklet as much as we enjoyed writing it, and that it will help you to get a better understanding of the challenges of phasing out fossil feedstocks, and your own role and perspective of action in this transition.

Harriëtte Bos, Daan van Es, Paulien Harmsen

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1 Introduction

1.1 Our climate and our materials

The effects of the ongoing climate change are becoming more and more visible in daily life. The additional amount of fossil carbon humankind can bring into the atmosphere before the 1.5 °C (the temperature rise the Paris agreement strives to stay below) is reached, is very small. It is becoming ever more clear that phasing out fossil feedstocks is essential for the survival of humankind.

The good news is that the introduction of a variety of new and innovative renewable energy technologies is taking up speed[1] and even parties that seemed to be grounded solid in the fossil world are beginning to redirect their investments towards significantly greener solutions.[2] All these changes, however, pose a new problem. The energy transition focuses on decarbonisation, away from the use of carbon-based energy carriers, but using sun, water and wind instead. However, carbon is the main ingredient of many of the materials we use every day. Examples of carbon-based materials we use are: all plastics, paper and board, all textiles, paints, many car parts, carbon-based building materials, a lot of our furniture, etcetera. The carbon atom is the essential atom in these materials and without it, they cannot exist. In many of the current materials the carbon comes from fossil feedstocks. Therefore, if fossil feedstocks, especially crude oil, are to be phased out, new renewable sources of carbon need to be found. For carbon based materials, a transition from fossil carbon towards *renewable carbon* as the new feedstock is urgently needed.

1.2 Renewable carbon for materials, where do we source it?

One of the first parties that advocated that there are basically only three sources of renewable carbon we can use for materials and chemicals is nova Institute.[3] They started their renewable carbon initiative in 2019, which aims to speed up the necessary transition.

The three sources of renewable carbon that are available to us are:

- biomass, which, next to being the main source of our food and an important energy source, can be converted into all kinds of chemicals and materials,

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[1] Hernieuwbare energie in Nederland 2019, CBS, 2020.

[2] https://edition.cnn.com/2020/12/18/investing/rockefeller-foundation-divest-fossil-fuels-oil/index.html

[3] nova Institute, Renewable carbon initiative, https://renewable-carbon-initiative.com/

- CO_2, which can be converted into all kinds of molecules, and subsequently into all kinds of materials,
- recycled materials, which can be converted back in a number of ways into new materials.

The transition towards renewable carbon for materials thus comprises three separate transition pathways, which are intrinsically different but at the same time also interconnected. An important point is, that none of the three pathways alone can provide all the feedstock we need for the production of the materials we use. All three pathways will be necessary in the future, and therefore development on all three pathways is urgently needed.

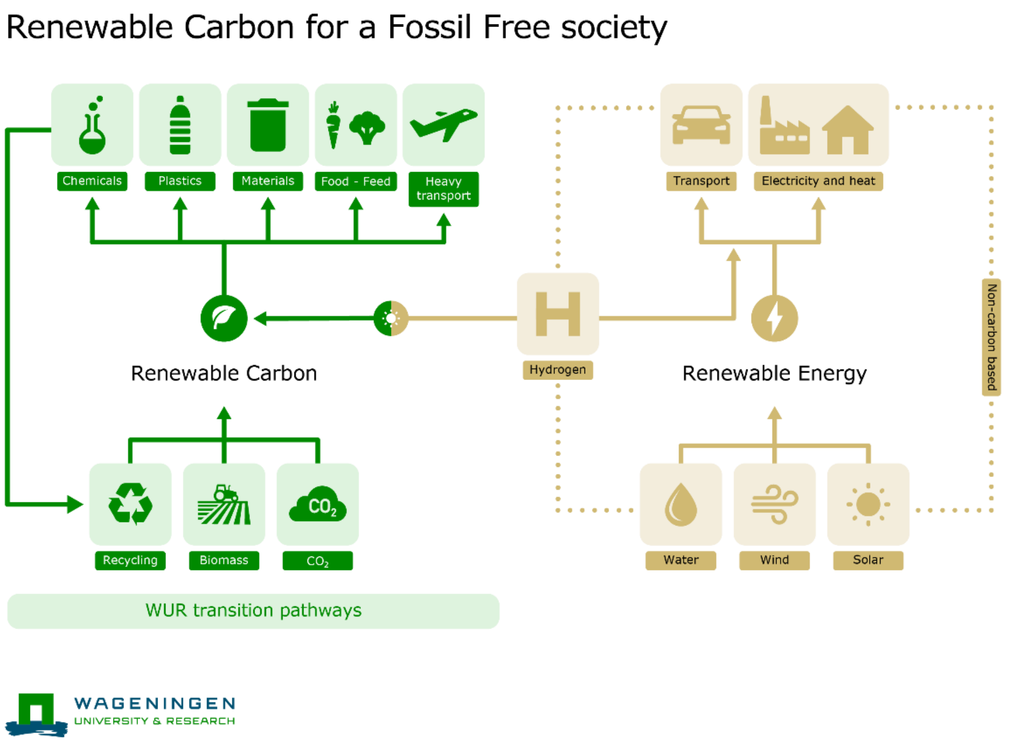

Figure 1.1. The three sources of renewable carbon for materials (on the left side), and the relation between the transition pathways to renewable carbon for materials and the energy transition.

As discussed in paragraph 1.1, our search for renewable carbon is intricately connected to the transition towards renewable energy, which aims at phasing out carbon as energy carrier. This overall system is presented in Figure 1.1, where not only the materials demand, but also the food demand, and the demand for heavy transport fuel (which cannot be easily electrified) are presented as the target applications for the renewable carbon transition pathways (left hand side of the graph). Hydrogen is in this vision seen as the most promising future option as energy carrier, and as we shall see in Chapter 4, hydrogen is also an important molecule for the CO_2 conversion processes towards chemicals and materials.

1.3 Relating to the bigger picture, the nexus extended

As touched upon briefly in the previous section, carbon is also the basic constituent of our food. Food security, now and in the future, is obviously high on the agenda of policy makers world-wide and NGOs, especially in the light of the ever increasing world population and the dooming climate change. Food security is often presented in connection with energy security and water security, as both water and energy are necessary for our food production. The Food And Agriculture Organisation of the United Nations (FAO) presents this as the water, energy and food security nexus, indicating that water security, energy security and food security are very much linked to one another, meaning that the actions in any one particular area often can have effects in one or both of the other areas.[4]

In this booklet we argue that the renewable carbon materials transition, striving towards renewable resource security, provides an additional entry point to the nexus, which cannot be seen separately from the other three entries. This extended picture is presented in Figure 1.2.

The transition towards renewable carbon materials in some respects brings us back to the pre-fossil feedstock era, however, we will need to rethink the whole production system including the production of materials in order not to compromise the other three entries of the nexus.

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[4] "Water-Energy-Food-Nexus" Food and Agriculture Organization of the United Nations.

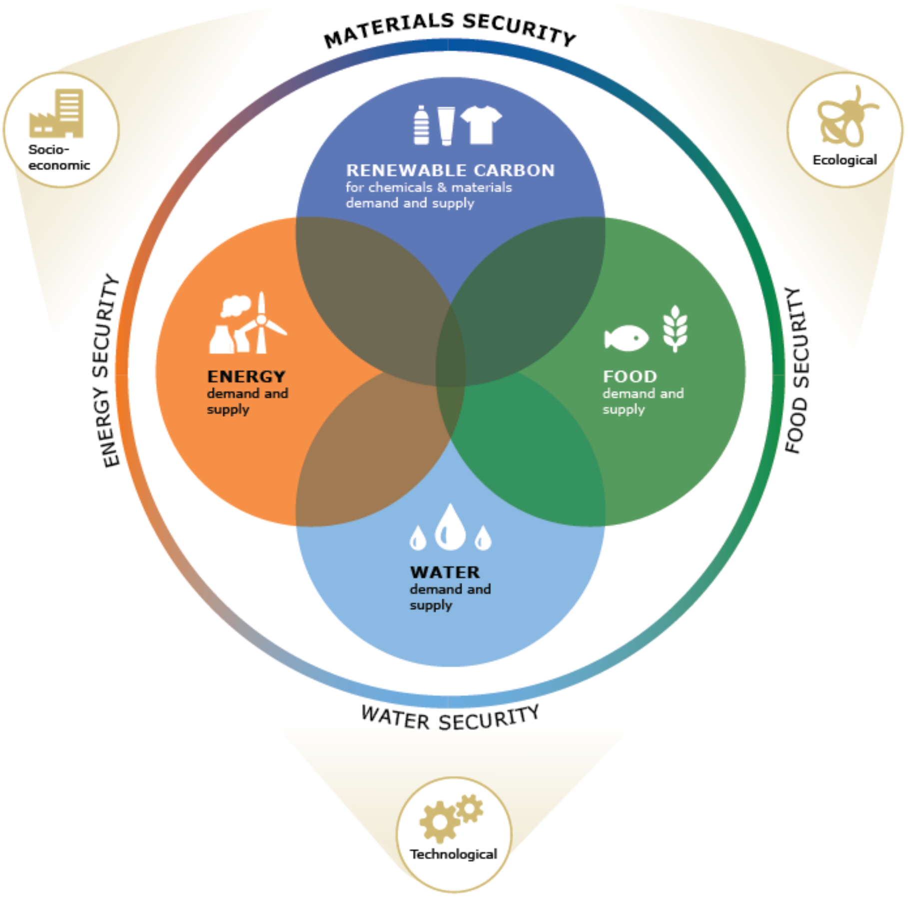

Figure 1.2 The renewable materials transition as integral part of the water food energy nexus: the water food energy materials nexus

1.4 History of carbon-based materials

For as long as we can remember, materials based on natural carbon such as flax and wood (in which the cellulose[5] polymer is the most important constituent) have been used as materials for clothing and construction. The industrial revolution led to the rise of the first (man-made) synthetic materials, which were still based on natural, non-

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[5] Cellulose is the main constituent of wood, see Chapter 3 for more background information.

fossil, resources. Celluloid, a material based on cellulose, was first developed in 1860 and was already being used as a replacement material for ivory around the turn of the century. Not long thereafter, rayon and cellophane, also based on cellulose, were introduced as materials for clothing and packaging.

In the first half of the twentieth century, a different type of polymers, produced from petrochemical raw materials such as crude oil and coal, became dominant. Materials made from these polymers have shown spectacular growth over the past century and are known as fossil-based synthetics or plastics.

Nowadays, materials based on renewable feedstocks are once again in the spotlight due to climate concerns and the declining crude oil supplies. Recent technological developments in, for example, industrial biotechnology and chemistry have extended the range of possibilities to produce these materials. Furthermore, these new renewable materials are supported by increasing concerns over the environment and plastic waste.

As discussed in paragraph 1.2 the renewable feedstock for these materials can be either biomass, CO_2, or recycled materials. In the next chapter the logic behind these three renewable carbon pathways will be presented and a picture will be drawn how the three pathways interconnect.

2 The build-up of carbon-based materials

2.1 Nature-based and man-made materials

In this chapter we make the distinction between nature-based materials and man-made materials. With nature-based materials we mean materials that are grown (generally as crops) and that we can apply in products by directly using the 3D structures or fibres coming from the crops or trees. With man-made materials we mean materials that are created in a (bio)chemical factory or plant by synthesising new chemicals and subsequently materials based on building blocks. These building blocks are presently often based on fossil feedstocks, but will in the near future be more and more based on renewable feedstocks (biomass, CO_2, or recycled feedstock).
Nevertheless, despite the very different ways these materials are produced, when you look deeper, all the way down to the molecular level, all these materials have a very similar general structure, and they have three fundamental things in common.

2.2 All carbon-based materials have three things in common.

The *first* thing that carbon-based materials have in common is their basic structure on a molecular scale. Both the nature-based and man-made materials are basically built up following the same principle[6]; they all exist of polymers. Polymers are extremely long chains (or networks) of connected atoms. The main atom in these chains is the carbon atom, often also oxygen and sometimes nitrogen are present. Next to that, all these chains contain a large amount of hydrogen atoms connected to the side of the carbon atoms. The long chain of mostly carbon and hydrogen we call the polymer backbone. Next to that, there are often a lot of other very small side groups connected to the backbone (see Figure 2.1). The polymer backbone together with the side groups forms the polymer. The exact composition of the polymer backbone and the side groups determines the properties of the materials; think of how strong they are, how stiff they are, how easily they shatter when they fall, if they dissolve in water or in another solvent, and if they melt or just decompose at higher temperatures.

The *second* thing that carbon-based materials have in common, is that they all started as CO_2 and water. Most often they were synthesised from these two molecules by micro-organisms or plants. In the case of nature based materials this was done recently. In the case of fossil feedstocks, this was done millions of years ago. And recently new

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[6] Strictly speaking this is not entirely true; diamond and graphite also consist of carbon (only carbon, no other atoms), but with a very different molecular structure.

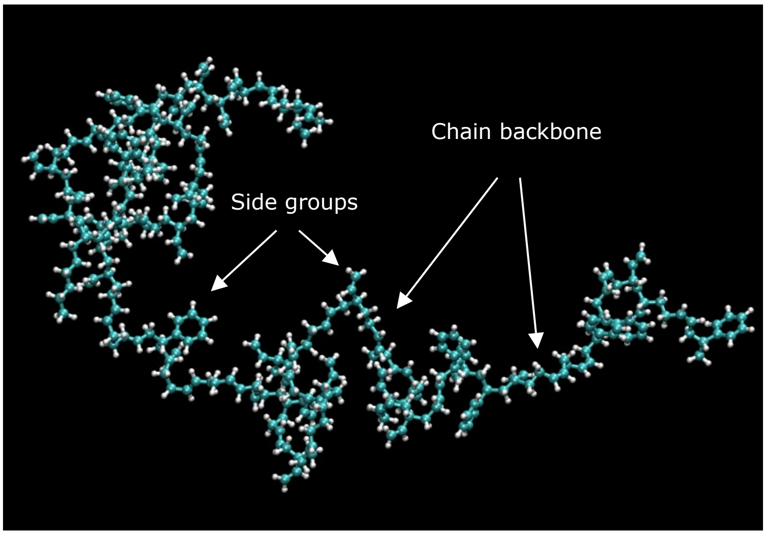

Figure 2.1 Small part of a polymer chain (in this case styrene-butadiene) from a molecular simulation. The chain backbone and the side groups are clearly visible. The blue-green dots are carbon atoms (diameter approximately 0,1 nm in reality) the grey dots are hydrogen atoms (graph by Gmrozz via Wikipedia).

routes are being developed by mankind towards carbon-based materials via the direct synthesis from CO_2 using chemical or biochemical processes.

The *third* thing carbon-based materials have in common is that they all need to be turned into a three dimensional (3D) structure before they are useful for producing a product; think of a fibre for textile, a plastic bottle, a paper sheet, or a wooden beam.

These three basic aspects are reflected in the way these materials can be produced and which stakeholders play a role in the production, now or in the future. Furthermore, they have implications for the way the materials can be recycled, and optimally turned into new products after they have reached the end of their service-life.

The next three paragraphs will elaborate further upon the implications of these facts for nature-based and man-made materials. We start with the first synthesis steps of CO_2 and water into small molecules, the building blocks (or monomers). Then the production of the carbon-based polymers from these building blocks will be described. Finally, the various methods that are applied to produce the variety of carbon-based (3D) materials will be presented.

2.3 Building blocks, the first step towards materials

Molecular building blocks, or in short building blocks, are the small molecules that form the starting point for carbon-based materials. They are not just any kind of chemical, they need to have a specific property: they need to have two reactive sides (chemical groups or radicals), which means a part on each side of the building block that can react with a reactive side of another building block. With just two reactive groups all the building blocks can link together to form a long molecular chain: the polymer (see Figure 2.2). Building blocks are also referred to as monomers.

2.3.1 Building blocks; nature-based materials

A plant uses the photosynthesis process to produce building blocks, such as glucose, from CO_2 and water, using sunlight as the energy source.

2.3.2 Building blocks; man-made materials

Similar to the photosynthesis process, chemical processes are being developed that convert CO_2 and water into small building blocks. These processes, however, need a lot of energy input, and are mostly still in an early stage of development, as will be explained in Chapter 4.

Another, more common, approach for the production of building blocks for man-made materials, is starting from a material that is already existing and breaking the bonds in the polymer chain, to end up with short building blocks. This is the approach in the present petrochemical industry, where the building blocks are produced from the fossil remains of plant biomass that was synthesised from CO_2 and water millions of years ago. This approach is also used when making man-made materials based on biomass (see Chapter 4) or when (chemically) recycling materials after their service-life (see Chapter 5).

2.4 Polymerisation, the second step towards materials

Once the building blocks are formed these can be used to produce the polymers. Producing polymers from building blocks involves a chemical reaction to link the building blocks together one by one which is called the polymerisation process. Often in a polymer chain a few hundred to up to more than 20.000 building blocks are linked together (see Figure 2.2, ‘n’ equals the amount of building blocks). The result resembles a very large plate of cooked very long spaghetti, but then about a million times smaller. Sometimes also building blocks with more than two reactive groups are used, in that

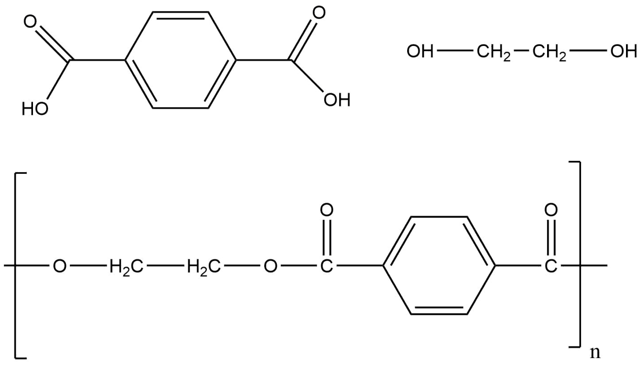

Figure 2.2 As an example the two building blocks of the polyester PET at the top, to the left: terephthalic acid, to the right: ethylene glycol. At the bottom the resulting polymer structure. During the formation of the bond between the two building blocks a water molecule is split off ('n' means this structure is repeated many times in the polymer, often between a few hundred up to several thousand times).

case the result from the polymerisation process is not a long chain but a network of polymer chains, more like a fishing net at a very, very small scale.

2.4.1 Polymers; nature-based materials

Plants, animals and microorganisms make polymers. Plants for instance produce starch and cellulose, polymers which are both made from the building block glucose. Animals produce proteins made from amino acids as the building blocks. Examples are keratin in wool and collagen in leather.

Another important polymer many plants make is lignin. This is an example of a polymer that is made from building blocks with more than two reactive groups. Lignin therefore has a netted structure which gives it a specific set of properties (see Chapter 4) Microorganisms sometimes also make other polymers such as PHAs, etc.

2.4.2 Polymers; man-made materials

The polymerisation process can be done in a chemical plant, to produce polymers that are well known from everyday life such as PET (polyester) of the plastic bottles and polyester clothing (Figure 2.2), or PE (polyethylene) from the plastic packaging bags. Most of these polymers are at this moment made from building blocks that come from fossil oil or gas. Therefore, these plastics are also referred to as fossil plastics.

When the building blocks that are used in the polymerisation process are made from biomass or were produced recently from CO_2 by micro-organisms, the polymers are referred to as biopolymers or bioplastics.[7] These bioplastics can be chemically identical to fossil plastics, but they can also be different (see Chapter 4).

2.5 3D structures, the last step towards materials

A polymer becomes a useful material when it is shaped into a three-dimensional structure.

2.5.1 3D structures; nature-based materials

Plants and animals produce 3D structures. The most important example of this is lignocellulose, a mixture of lignin and cellulose, the material that wood and many plant stalks are made of. Another example are the cellulose fibres, such as cotton and flax and animal fibres such as wool. Man-kind has used wood and fibres since ancient times for the production of all kinds of textiles, household applications, building materials and other products. In this case we just use the 3D material structure that the plant or animal has produced, and turn it into a product by either mechanical processes such as spinning, weaving and sawing, or by an isolation process such as used in the production of paper pulp for paper and board.

2.5.2 3D structures; man-made materials

For man-made plastics, either fossil or biobased, many polymer processing technologies are used these days; extrusion, fibre spinning (for textiles and non-wovens), producing thin films (for cling film, packaging foils or plastic bags), injection moulding of small or large products (from buttons to computer housings to complete one-piece sun-loungers), etc. These technologies can be applied because many of the man-made fossil and biobased plastics can melt at higher temperatures and can then be formed into the specific shape, which subsequently sets when the plastic is cooled back down. Other processes are applied when polymers cannot melt, but can be dissolved. Such processes are used in the production of viscose fibres and cellophane, for instance.

2.6 The relevance for renewable materials

In this chapter we explained the differences between building blocks, polymers and 3D structures. The question now is, which steps are needed to produce our materials, using

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[7] Note that even though these materials are made from biomass, they are still referred to as man-made, because the production into the polymer is not done in a living organism, but in a chemical factory.

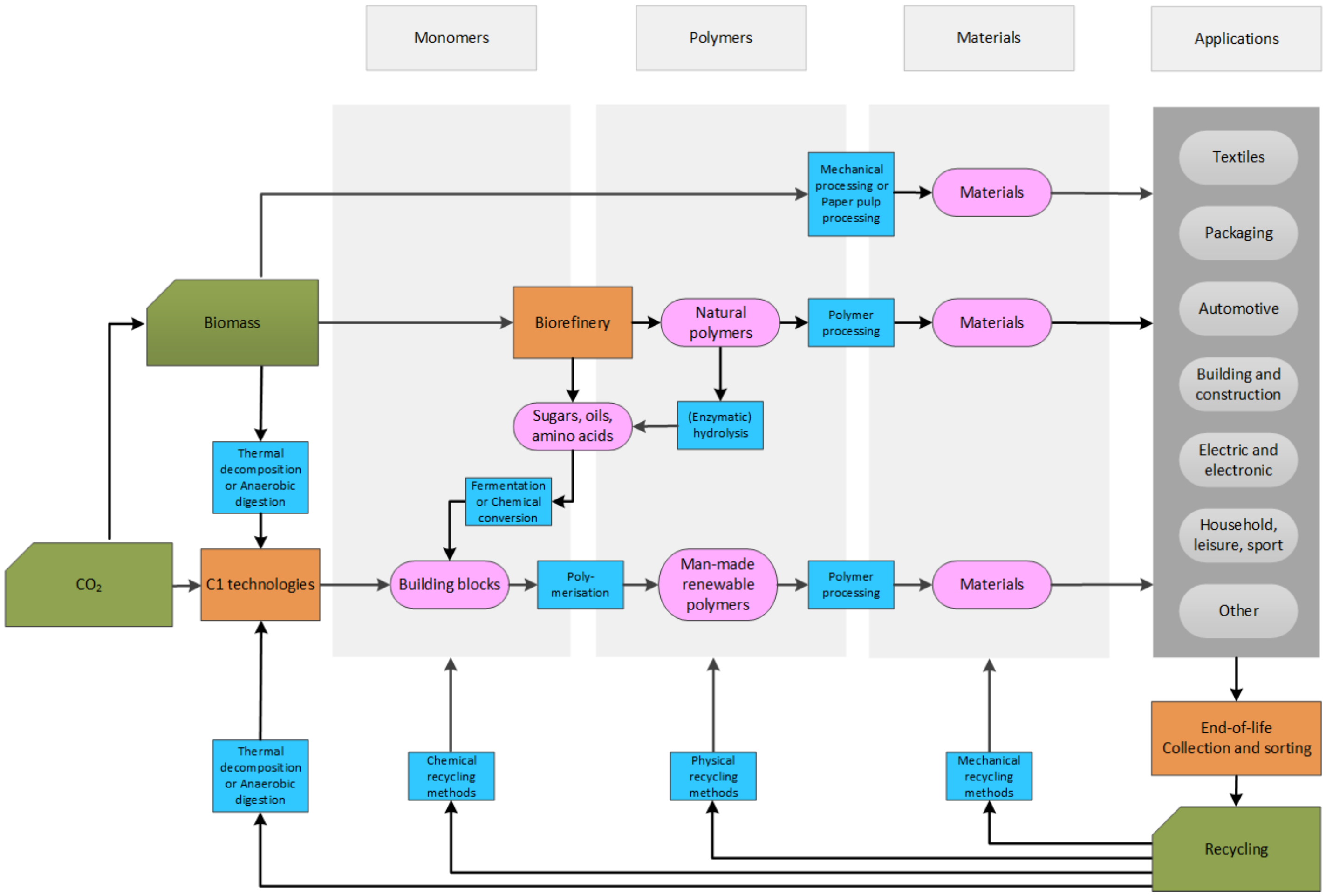

Figure 2.3 Schematic overview of the renewable carbon-based production system with focus on materials.

one of the three sources of renewable carbon: biomass, CO_2, or recycled materials. How do these steps differ and where do they coincide?

A schematic overview of the total renewable carbon-based system is presented in Figure 2.3. This overview serves as a guideline in the next three chapters, and gives a comprehensive overview of the total (renewable) carbon based system. For easier reading of the next chapters it is worthwhile to familiarise yourself with the structure of the scheme.

The underlying structure of carbon based materials, as discussed in this chapter, is presented in the grey columns from left to right: the building blocks (denoted as monomers), polymers and materials are shown in the consecutive light grey columns, the darker grey column at the right hand side comprises all the applications that can be produced from carbon based materials.

The production routes starting from the three sources of renewable carbon are presented in horizontal direction. The feedstock, intermediate products and the processes are shown in the different coloured boxes. The starting points of the three different pathways are presented by the green boxes; the orange boxes indicate the core processing steps of the three different pathways. In the pink/purple boxes the specific intermediates are presented and in the blue boxes other processing steps are shown. The arrows show the possible pathways that can be followed to produce a material, please note that the arrows have a specific direction, indicating a specific order in which the processing steps are generally applied.

There are a few instances where different processing steps can lead to the same type of intermediate, as indicated by the connecting arrows. This is especially the case for the building blocks, which can be produced starting from each of the three feedstocks, biomass, CO_2, or recycled material.

In the next three chapters we will dig deeper into the three pathways towards renewable carbon: starting from biomass in Chapter 3, from CO_2 in Chapter 4 and from recycled materials in Chapter 5. In each of these chapters the schematic overview presented in Figure 2.3 will be used as the general framework, and the specific pathways will be highlighted.

3 The Biomass pathway, using biomass for materials

3.1 Introduction, what is biomass[8]

Biomass is the substance of which living and dead organisms are composed. This implies biomass is not limited to plants; animals and micro-organisms are also composed of biomass. An overview of important biomass types and products, focusing on plants and micro-organisms, is presented in Table 3.1. Apart from the so-called primary products, that we extract for use in many applications, the processing of biomass leads to various by-products, which are also used for specific applications. Both are presented in Table 3.1. Our food is thus made from biomass, as is the feed of our livestock, but we have also used biomass since prehistoric times as source for energy and materials. More recently, transportation fuels based on biomass were developed.

Table 3.1. Some biomass types; specifying current products and by-products.

Biomass type	**Primary products**	**Important secondary products**
Forestry trees	Wood, cork, resin, latex	Foliage, sawdust, bark
Landscape management plants, trees and grass	Wood, aquatic plants, roadside plants	Pruning waste
Crops		
• Grain (wheat, corn…)	Grain kernels, starch	Straw, bran, chaff
• Oil crops (rapeseed, sunflower…)	Beans, nuts, oil	High-protein leftover pulp, pruning waste (wood)
• Sugar beet	Sugar	Sugar beet pulp, molasses, sugar beet crowns, sugar beet leaves
• Potatoes	Potatoes, starch	Potato pulp
• Oil palm	Palm oil	Variety of large quantities of residue streams
• Fruit and vegetables	Fruit and vegetables	Stalks, foliage, fruit and vegetable waste
• Meadow grass	Grass, hay	
Microalgae, seaweeds	Oil, protein, hydrocolloids	Cell wall residues
Residue streams after consumer and animal use	Organic waste, old paper, manure, waste fat, waste cooking oil, swill, discarded textiles and sewage sludge	

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[8] Adapted from: Johan van Groenestijn, Paulien Harmsen, Harriëtte Bos (2019) Biomass for the circular economy, everything you wanted to know about biomass but were afraid to ask, Wageningen UR.

For use as materials, originally biomass was applied for its structure (such as wood, linen, cotton), but these days we apply a wide range of technologies to use the biomass as feedstock for many different materials applications. In the next paragraph an approach to classify various uses of biomass for materials, based on the line of logic discussed in Chapter 2, will be presented.

3.2 Three different ways to use biomass for materials

There are three different ways to use biomass for materials applications:

- As *nature-based materials*; using the 3D material structure that plants, animals or trees have built, such as fibres and wood
- As *natural polymers*; using the polymers that plants or micro-organisms synthesise, such as starch, cellulose, keratin and lignin for the production of a variety of materials

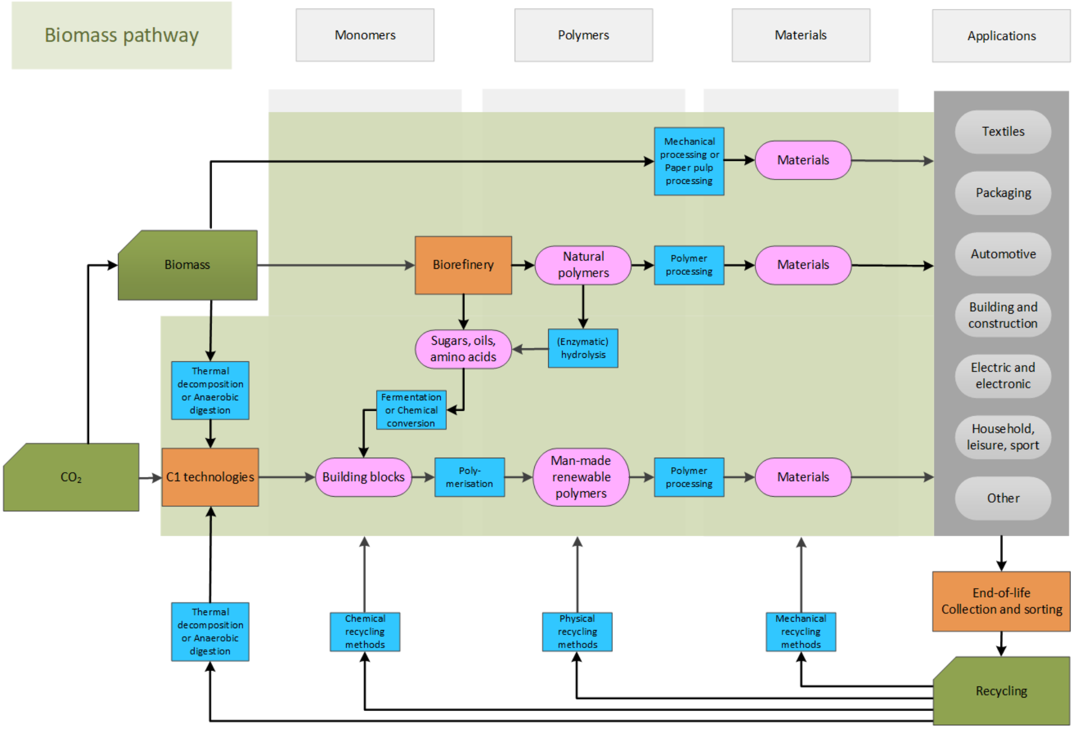

Figure 3.1. The renewable carbon-based system, focusing on possible pathways starting from biomass (light green). (See Paragraph 2.6 for an explanation of the general structure of the scheme).

- As *building blocks*: breaking down the natural polymers, or the carbohydrate or oil components, towards building blocks and use these to synthesise new chemicals and materials, such as (man-made) bioplastics.

These three different ways principally relate to the three basic steps that are needed to produce materials which were discussed in Chapter 2. The approaches are presented (highlighted in light green) as part of the total renewable carbon system in Figure 3.1.

Generally, these three approaches apply different processing techniques, and they also differ in the type and number of stakeholders involved in the production processes. This is discussed further in the following three sections.

3.3 Biomass for 3D material structure

Mankind has used biomass for the material structure it provides since very early days. An important application has always been as fibre. The craft of spinning fibre into yarn and weaving yarn into cloth is essential for the production of clothing, ropes and strings. Flax, the feedstock for linen, is used since thousands of years. At excavation sites of Stone Age dwellings in Switzerland, dated at approximately 7000 B.C., flax seeds, twines and fishing nets were found.[9] Other examples of fibre crops in use today include cotton,

Figure 3.2. Leather has a high environmental impact during production, but its products may last a lifetime.

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[9] A. Leseigneur, Lin des Ville Line des Champs, Association pour la Valorisation du Patrimoine Normand, Elboeuf, France, 17.

hemp and jute. (For an extensive overview of fibre resources see Textile for circular Fashion part 2.[10])

Animal derived materials include wool, leather (Figure 3.2) and fur, in the past used for warmth and protection. The market for fur is relatively small and there is a strong societal pressure to phase out fur completely. Both leather and wool are applied more widely. Even so, the wool market is only a very small part of the total textiles market. Leather and sometimes also wool is seen as a by-product of meat production. Both these materials give rise to high greenhouse gas emissions during production compared to plant-based products. However, animal products like wool and leather have unique properties and can last a lifetime, which drastically reduces their environmental impact over the complete lifespan.
A special animal product is the catgut or gut, used for the production of violin and cello strings and which, unlike the name might suggest, is not made from cats but usually from sheep or goat intestines.

Another important application of fibres is in paper and board. These fibres are often produced from wood, but other cellulosic biomass sources such as grass, straw, etcetera, can also be used. Some of these are presently under development.

Figure 3.3. Wood has a myriad of applications in materials (Photo: Arjen Bosch).

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[10] Paulien Harmsen, Wouter Post, Harriëtte Bos (2022). Textile for circular fashion. Part 2: From renewable carbon to fibres, Wageningen University & Research.

Next to fibres, wood (Figure 3.3) as a structural material is important for building and construction applications, furniture, tool handles etcetera. These days wood as a building material is experiencing a revival due to the fact that wood is capable of storing carbon for a long time and has a far lower CO_2 impact than concrete or steel.

Crops and trees may supply smaller parts, such as straw, cork, chaff and chips, that can be used for many applications e.g. fibre boards, flooring, etcetera.

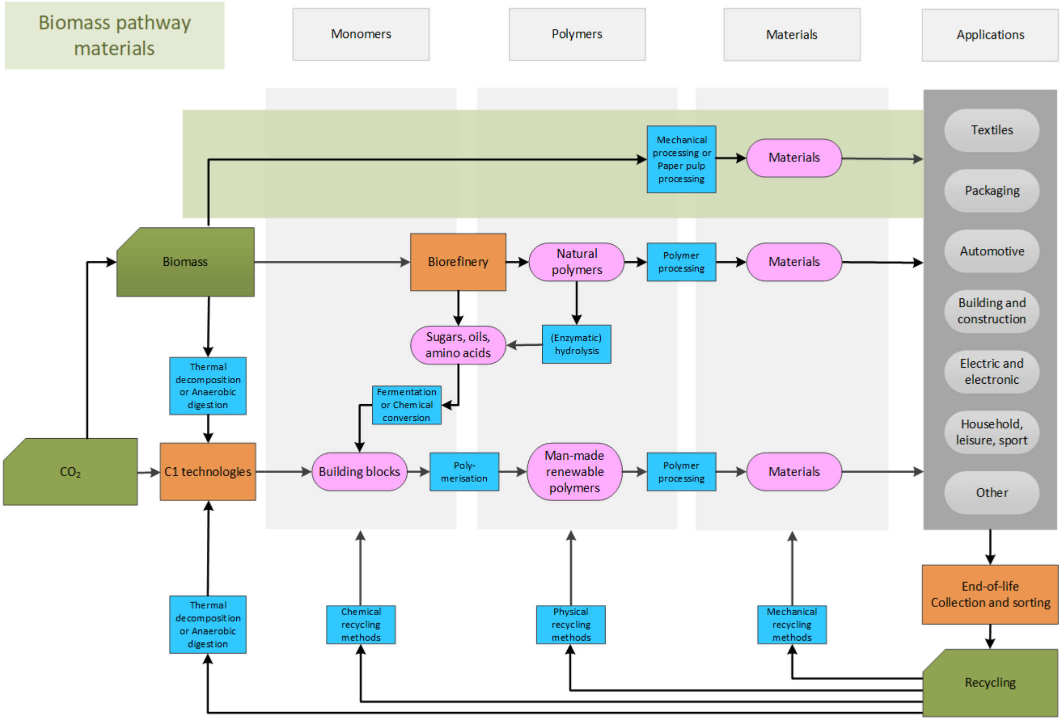

Figure 3.4. The renewable carbon-based system, the pathway of biomass for 3D material structures (light green).

The production of all these biomass-based types of products often requires many, mainly *mechanical*, processing steps (see paragraph 2.5.1). Stakeholders active in the production chain vary from craftsmen producing furniture or music instruments to large scale sawmills, furniture factories or spinning and weaving mills. The 3D material structure of the biomass is used directly in the product and in the overall schematic representation these production routes are placed at the top. (See Figure 3.4).

The exception to the application of mainly mechanical techniques is the production of paper and board, which requires the separation of cellulose fibres from the lignocellulose structure (see next paragraph). Therefore, this is often done in a combined chemical/mechanical process, and generally at large scale.

Even though these applications partly date from ancient times, it does not mean there is no room for innovation and development. An important research topic is the further optimisation of (non-food) crops by breeding for higher yields, stronger and longer fibres, or for easier separation of (hemi) cellulose and lignin. Multifunctional crops, which can supply feedstock for many applications and are efficient in land and input use, are also targeted by breeding developments. Furthermore, using other crops and side streams (crop parts) for paper and board production or textiles is an important subject of development.

3.4 Biomass as supplier of natural polymers

Biomass contains many components which play a specific role in the physiology of living organisms. Table 3.2 presents the most important examples.

Table 3.2. Biomass components and their function.

Component	**Function**
Carbohydrates	
• Cellulose	Part of cell walls (rigidity and compartmentalisation)
• Hemicellulose	
• Pectin	
• Hydrocolloids	
• Starch	Energy storage substances
• Sucrose	
Lignin, suberin	Part of cell walls
Proteins • Storage proteins • Collagen • Keratin	Biocatalysts (enzymes), temporal storage of amino acids for use in subsequent phases of growth, structural components in animals (muscles, tendons)
Fat, oil	Reserve substances

A number of these components are natural polymers: starch, cellulose, hemicellulose, lignin and proteins such as collagen, keratin and many others. Although a variety of applications is developed by mankind over the years, the present applications of materials based on the natural polymers pathway is relatively limited compared to the abundant availability of wood and natural fibres in our daily lives. Nevertheless, interest in a number of these materials, viscose and lyocell (based on cellulose) for instance, is growing.

Many of the parties involved in the development of these categories of materials have their roots either in the agri-industry or in the paper industry, which both have as their core activity the processing and separation of biomass into separate components through biorefinery processes (see Figure 3.5).

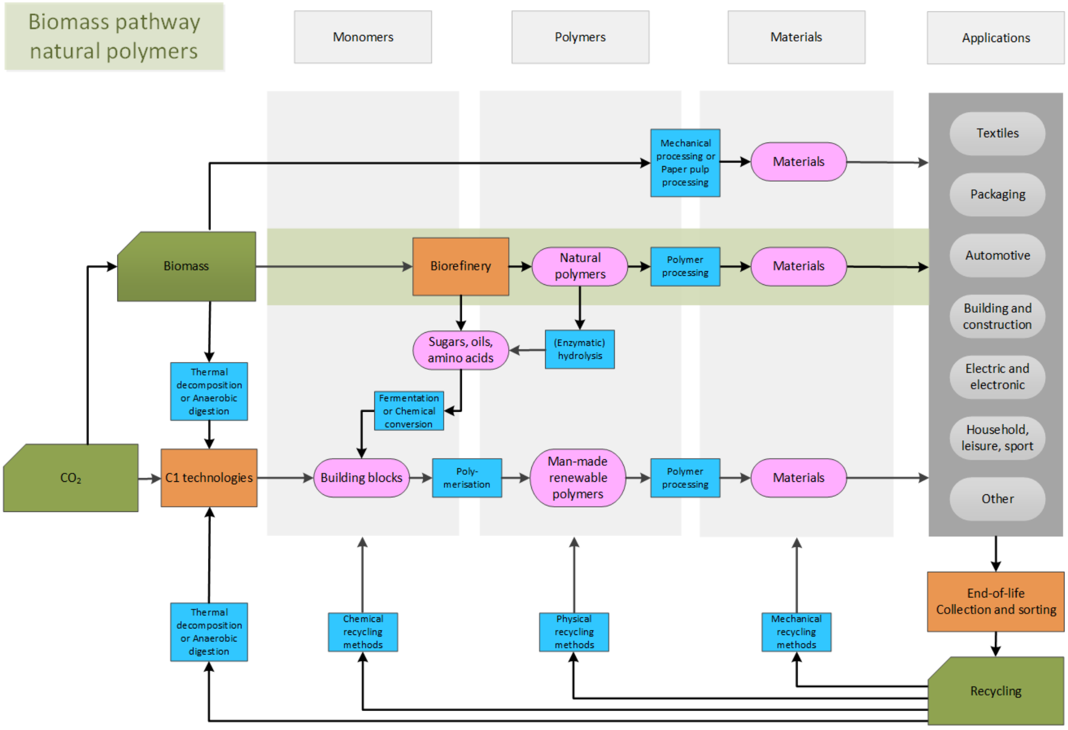

Figure 3.5. The renewable carbon-based system, the pathway of natural polymers from biomass (light green), towards 3D material structures.

The decisive difference between this biomass pathway and the examples from the previous section (3D materials), is that in the natural polymers pathway *physical processes* (mostly dissolving or melting, or both) are used to isolate the natural polymer (biorefinery) and to bring it into the desired 3D shape through polymer processing (See

Figure 3.5). Sometimes, in the biorefinery processes also some chemical modification steps are required.

The first applications exploiting the polymeric structure of these components were developed several thousands of years ago. An early example is their use in glue, more specific animal glue. The first known written procedures of making animal glue date from approximately 2000 BC.[11] Between 1500 and 1000 BC it was used for wood furnishings and is found on the caskets of Egyptian Pharaohs. The use of hide glue for building violins evolved with the development of the violin family since the 16th century, and hide glue is still the glue of choice for modern luthiers (See Figure 3.6). Another ancient example of the use of a natural polymer as a glue is the use of starch for gluing papyrus.

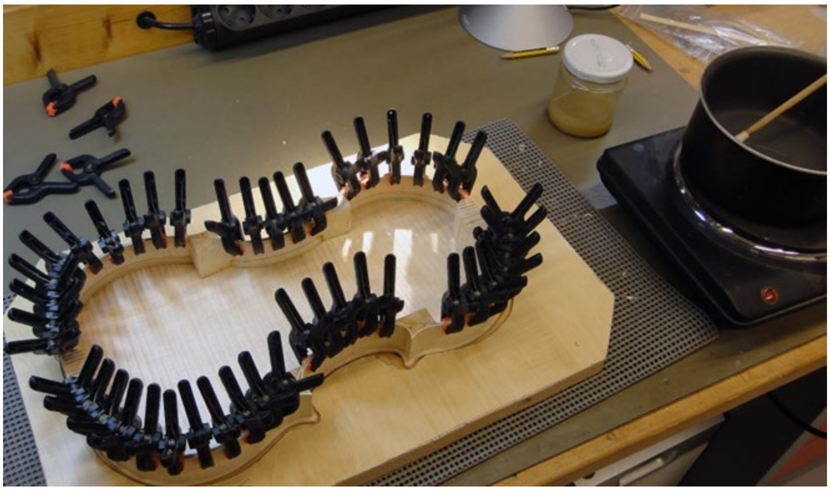

Figure 3.6. Hide glue (in the glass jar) is still the glue of choice for modern violin makers as its properties are unmatched by synthetic glues. (Photo: Arjen Bosch)

New applications of natural polymers for structural materials have been developed in the last century. These are based on the increased scientific insights into chemistry and the behaviour of polymeric materials gained since the late 1800s. Examples are:

Cellulose: the use of cellulose in polymeric applications was made possible by the development of the viscose process, patented in 1894,[12] for making so-called

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[11] Wikipedia, animal glue: https://en.wikipedia.org/wiki/Animal_glue

[12] https://en.wikipedia.org/wiki/Rayon

regenerated cellulose, such as viscose fibres and cellophane. The viscose process leads to materials that are entirely made up of cellulose polymers, but can be processed into thin films and a variety of textile fibre structures. In 1982 Lyocell entered the market, which is also a fibre based on cellulose. The process is different from the viscose process. It uses far less chemicals and has a much better environmental profile (Figure 3.7).

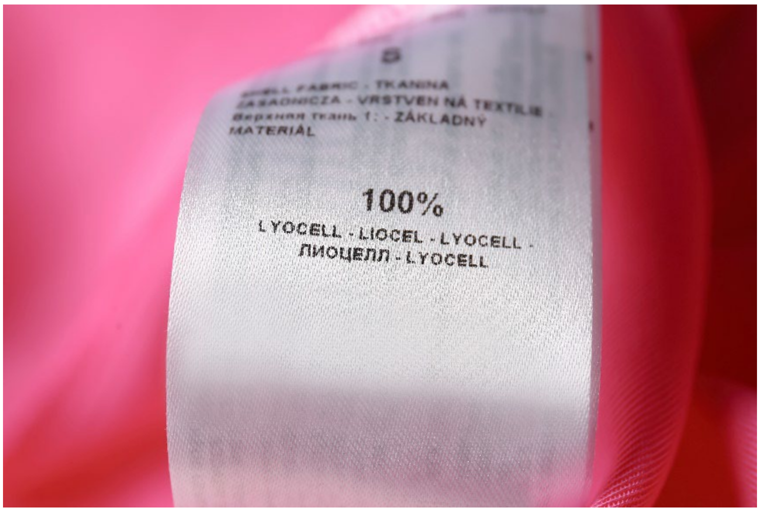

Figure 3.7. Lyocell is a textile fibre produced from cellulose, with a process that is more environmentally benign than the viscose process.

Starch: Over the last 30 years numerous biobased plastics based on starch have been developed. Examples of starch-based plastic products are: packaging films, mulching films, bin-liners, plant pots, cutlery and plates. Many of these products have entered the market in the last decades, but their total volume is still relatively small. The large asset of these materials is that they can be composted or (anaerobically) digested, which makes them advantageous especially in short term applications in combination with food or agricultural products.

Lignin: a very recent example is the use of lignin in asphalt, where the polymeric lignin structure is able to effectively replace bitumen.[13] Other lignin applications focus on using it as a replacement of phenol in PF (phenol formaldehyde) resins, used in building applications.

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[13] Lignine, groene grondstof voor chemicaliën en materialen, Jan van Dam, Paulien Harmsen, Harriëtte Bos, Richard Gosselink (2017) (in Dutch).

The main advantage of these materials based on natural polymers is that they are in principle inherently biodegradable, and that they can be formed into shapes and structures, like endless fibres, thin films, and thin walled moulded parts that cannot (or in some cases only with a lot of effort) be produced by the mechanical processes presented in the previous paragraph. Main disadvantage is that isolation of these natural polymers from their complex natural matrix can be difficult and costly, especially when high purity polymers are desired. Another disadvantage is that due to the specific (molecular) structure of the natural polymers it is sometimes difficult to reach a desired properties profile, to make the material suitable for a wide range of applications. One of the properties of starch polymers for instance is their water sensitivity, in some applications -together with their biodegradability- this can be exploited as an advantage, but it also limits the possible application area of these materials.

Innovation is focused on various topics. For example, on new, more environmentally benign processes for (regenerated) cellulose fibres, but also on alternative cellulose resources (besides wood). Additionally, improving properties of starch-based plastics is ongoing, as well as extending the application area of lignin in for instance resins and all kind of binders.

3.5 Biomass as feedstock for producing building blocks

The decisive difference between this biomass pathway and the examples from the previous two sections is that in this case first the biomass components are broken down into building blocks. Subsequently, *(bio)chemical polymerisation processes* are used to turn the small building blocks into a new (biobased) polymer (Figure 3.8). After that, the standard polymer processing techniques are applied[14] to form the polymers into the desired 3D shape, whether it be a fibre, a film, or a moulded part. These processing techniques were mostly developed for fossil based polymers, and are generally based on physical processes (mostly melting, mixing, dissolving or a combination of these).

Even though there are a few applications in which the natural polymers have excellent properties that cannot be reached by man-made (bio)polymers (see the previous paragraph), generally it can be stated that the building blocks route gives much more freedom to design a material with exactly the desired properties profile.

Building blocks can be made from different biomass components: (all kinds of) sugars, starch, oils and fats, cellulose or hemicellulose. First, these components need to be isolated from the biomass. Then they have to be broken down into a small intermediate component (often glucose). This intermediate component can then be turned into

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[14] See paragraph 2.4 for a short overview of polymer processing techniques.

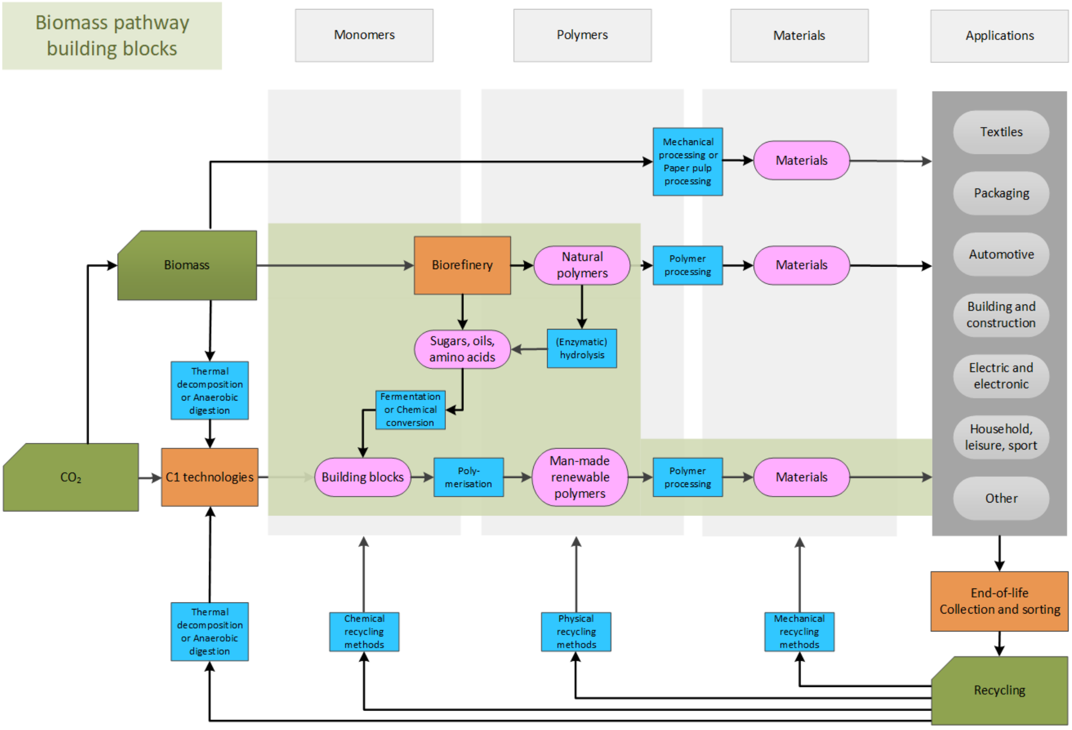

Figure 3.8. The renewable carbon-based system, building blocks from biomass (light green), towards man-made polymers through polymerisation and 3D material structures.

building blocks with two reactive groups by (bio)chemical processes.[15] Many different building blocks can be produced in this way, which can subsequently be polymerised into many different kinds of polymers. The polymers are produced from the building blocks by polymerisation reactions in a chemical plant and we thus refer to them as *man-made (bio)polymers*.

Two important aspects of the building blocks approach are discussed below: the kind of building blocks that are produced, and the types of reactions used to produce the building block.

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[15] Technically, the reactive group can not only be a chemical side group, such as is the case in for instance the building blocks for PET, it can also be a radical. This second option occurs in the case of a double bond that breaks open during the reaction, to form two radicals.

3.5.1 What kind of building blocks are produced?

Two choices can be made regarding the kind of building blocks: Production of drop-ins or production of new building blocks and polymers.

Production of drop-ins

For *the drop-in approach*, building blocks are produced from biomass that are chemically identical to building blocks presently produced from fossil feedstocks. Through this approach, polymer materials can be made that are chemically completely identical to the presently used fossil-based polymers. The advantages are that they can be processed with the same processes, recycled and even mixed with the fossil-based materials, furthermore they can be applied in the applications and through the processes that are already in place and no additional investment or development is needed. The main difference is that instead of fossil-based these materials are based on renewable feedstocks.

An extensive overview of possible production routes, starting from biomass, towards the currently applied (fossil based) polymers, is presented in an earlier publication in this series.[16] Whereas these biomass-based materials can be applied directly, they do compete against their fossil counterparts. In case the production costs of the drop-in biomass-based building blocks are higher (which is often the case due to currently still smaller production scale), they will have a tough job outcompeting their fossil counterparts and may require additional support by policy measures e.g. a carbon tax, or a mandatory percentage of bio-based feedstocks to reach the market. Furthermore, the building blocks that can be made cheaply and at large scale from fossil feedstocks are not necessarily the preferred building blocks to be produced from biomass.[17]

Production of new building blocks and polymers.

The *new building blocks* approach focuses on building blocks that are different from the fossil-based building blocks. And consequently, also the polymers produced from these

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[16] Green building blocks for biobased plastics; Biobased processes and market development, Paulien Harmsen, Martijn Hackmann (2012).

[17] See for a more in-depth explanation: Duurzaamheid van biobased producten; Energiegebruik en broeikasgas-emissie van producten met suikers als grondstof, Harriëtte Bos, Sjaak Conijn, Wim Corré, Koen Meesters, Martin Patel (2011) or the related paper in English: Accounting for the constrained availability of land: A comparison of bio-based ethanol, polyethylene, and PLA with regard to non-renewable energy use and land use; Harriëtte Bos, Sjaak Conijn, Wim Corré, Koen Meesters, Martin Patel, Biofuels, Bioproducts and Biorefining Volume 6, Issue 2, Pages 146 – 158 (2012).

Early examples

Early examples, which in view of the structure presented in this booklet apply a slightly hybrid approach, are the use of natural oils in paint and the production of natural rubber. In both these cases natural building blocks or polymers (either oils or latex) are applied which are cured into a netted polymeric structure. In the case of the early paints and varnishes this curing process is driven by ambient oxygen, which is gradually taken up. In the case of natural rubber, the polyisoprene polymers in the latex are cross-linked by adding sulphur, a process called vulcanisation, which was developed by Charles Goodyear as early as 1839.
In both cases the resulting polymer has a netted structure after it has been shaped, and can therefore not again be molten or dissolved.

building blocks are different. This implies they can have interesting new properties compared to the drop-in polymers, but they may also require much additional effort in order to further develop and support their application. Also market introduction of new types of materials may require registration through REACH,[18] and other product related certification schemes, which also generally serves as a barrier. This obviously takes time and money and may make the introduction of the new building blocks a long journey.

Both the drop-in polymers and the new-building-block polymers are produced by polymerisation reactions in a chemical plant and we thus refer to them as man-made (bio)polymers.

3.5.2 What kind of reaction routes can be used to produce the building blocks?

Production of the building blocks and the polymers from biomass feedstock can be done in a number of ways: via micro-organisms (including anaerobic digestion), via (man-driven) chemical reactions, or via thermal decomposition.

Microorganisms producing building blocks

The use of biotechnology, in which micro-organisms, for instance yeasts or bacteria, convert a biobased feedstock such as sugar or starch in another molecule is very old. These days several interesting building blocks that are subsequently used to produce a polymer are made in this way. An important example is lactic acid, which is the building block for the polyester PLA (Figure 3.9).

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[18] REACH is the European regulation on chemicals. REACH stands for Registration, Evaluation, Authorisation, and Restriction of Chemicals.

Biotechnological routes are generally done in water, at relatively low temperatures and one of the challenges is to get the desired molecule separated from the reaction mixture. A relatively recent development is the application of enzymes, isolated from the micro-organism, as a catalyst for chemical conversions. Utilizing natural or modified enzymes to perform organic synthesis is called chemo-enzymatic synthesis. These reactions are very specific, they can be used to produce molecules that are otherwise difficult to create.[19]

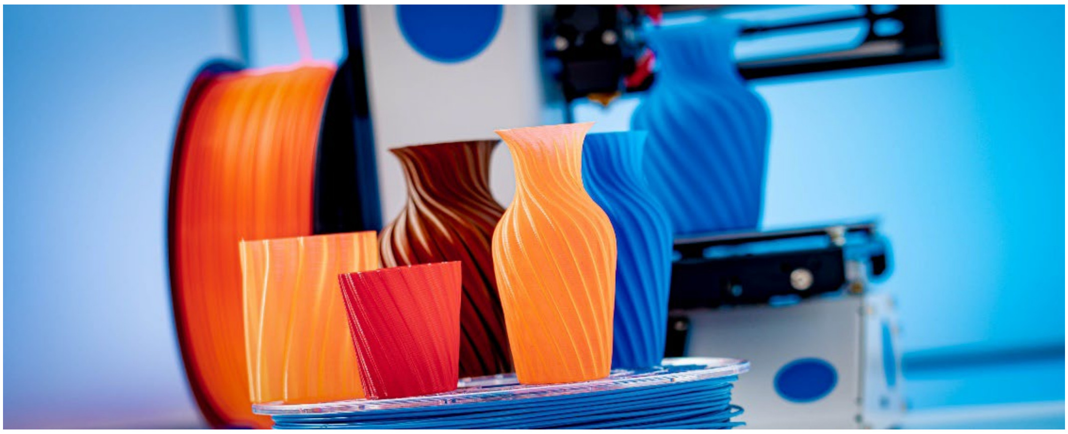

Figure 3.9. PLA is well established as material for the filaments used in 3D printing.

Microorganisms producing polymers

In some cases the micro-organism is able to produce not just a building block, but the complete polymer. A rather successful example development are the PHAs (polyhydroxyalkaonates), polyesters which are produced by numerous micro-organisms (Figure 3.10). PHAs span a very wide range of properties, because many different monomers (building blocks) can be built-in in the polymeric structure, depending on the type of microorganism and the cultivation conditions applied. The micro-organisms need to be fed with a carbon source, carbohydrates such as glucose and sucrose can be used, but also vegetable oil or glycerine (from biodiesel production) are suitable sources.[20] Furthermore, even sludge from wastewater treatment and other waste streams can be used, making the production of PHAs a method to truly upcycle waste streams. After

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[19] See for an extensive review: Fermentation for the production of biobased chemicals in a circular economy: a perspective for the period 2022–2050 - Green Chemistry (RSC Publishing)

[20] This pathway differs from the direct CO_2 conversion pathway described in the next chapter. For PHA production first the separate production of the biomass feedstock is needed.

Figure 3.10. Cutlery made of PHA. PHAs are compostable (in home composting also) and biodegradable in anaerobic fermentation plants, soil and even in the marine environment.

production, the polymers need to be separated from the microorganisms by downstream processing (DSP), which can be costly.

Chemical reactions producing building blocks

The conversions in chemical reactions generally use catalysts that are mostly based on inorganic molecules, and that increase the reaction rate. Chemical reactions can be used to produce a wide range of building blocks. An important example is the production of FDCA (furane dicarboxylic acid) which is one of the building blocks for the new polymer PEF (polyethylene furane 2,5 dicarboxylate) which is seen as a biobased alternative for PET). Many other examples exist, such as the production of ethene (a typical drop-in) from ethanol and the subsequent production of PE (polyethylene). Chemical reactions are generally done in a water-free environment at high temperature.

Thermal decomposition or anaerobic digestion for producing building blocks

Thermal decomposition (breaking down biomass at high temperatures) or anaerobic digestion (breaking down biomass by micro-organisms) of carbon-based feedstock can lead to precursors of building blocks. This can be followed by eventual synthesis of the building blocks and subsequently the polymerisation step. Thermal decomposition can be applied in the case of very mixed feedstocks that is not suitable as raw material for the processes described above. An example is the process of bioBTX for the production of aromatic building blocks[21] through catalytic pyrolysis of biomass.[22] Anaerobic digestion can be used in the case of mixed, wet feedstocks. If the decomposition is all the way down to CO or CO_2 the follow up processes are identical to the ones described in section 4.3.

3.5.3 Mixing fossil and renewable building blocks

The building block route also gives the opportunity to use building blocks from both fossil and renewable origin: for instance, the PlantBottle™, that was introduced by among others CocaCola over a decade ago, was made from bioPET with 30% renewable content.[23] These materials can be considered as a transition step towards fully renewably based materials. As an example, CocaCola announced at the end of 2021 that they have now produced a prototype of a one hundred percent plant based BioPET.[24]

3.5.4 Biodegradability

A number of the man-made biopolymers are also biodegradable, but not necessarily so. The drop-in biopolymers are only biodegradable if their fossil counterpart is, which is the case for only a few. Many of the materials based on new building blocks are biodegradable, but not all. In contrast, all natural polymers discussed in section 3.4 are biodegradable. More background on the stage of development of drop-in and new building blocks based polymers can be found in this series publication on biobased plastics.[25]

3.6 Different complexity of the three biomass approaches

Generally speaking, the three biomass-based routes (nature-based materials, natural polymers, building blocks from biomass) have an increasing level of complexity in number of stakeholders involved and number of technological and chemical processes involved. This is presented schematically in Figure 3.11 (The thermal decomposition and anaerobic digestion routes are not shown in this diagram).

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[21] Aromatic building blocks contain ring structures, such as the ring in terephthalic acid (see Figure 2.2).

[22] This process can also be used for waste plastics (see Chapter 5.4).

[23] PET is made of two alternating building blocks: ethylene glycol and terephthalic acid. In the PlantBottle™ only the ethylene glycol was plant based (approximately 30% of the polymer weight).

[24] https://www.coca-colacompany.com/news/100-percent-plant-based-plastic-bottle.

[25] Biobased plastics 2020, Karin Molenveld and Harriëtte Bos (2020).

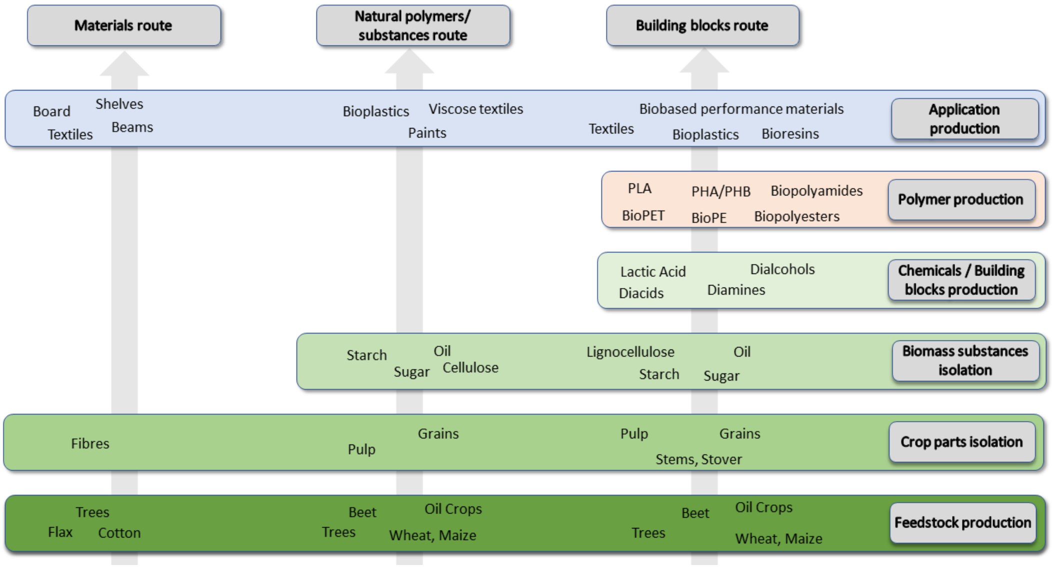

Figure 3.11. The complexity of the production chain and the number of stakeholders involved differs for the three different approaches to use biomass for materials. Each horizontal bar represents at least one type of stakeholder, ranging from feedstock production at the bottom to application production at the top.

And whereas for the nature-based materials and natural polymers route production chains have often been in place for decades, the building blocks route requires cooperation between many stakeholders that may come from different sectors, such as the agri-food sector and the chemical sector, which makes cooperation much more demanding. In Chapter 6 we will elaborate further on this complexity.

4 The CO_2 pathway towards materials

4.1 Introduction

CO_2 has become synonymous with climate change as it is one of the greenhouse gases that induce the warming up of the atmosphere. Therefore, a number of technologies are presently being developed to remove CO_2 from the atmosphere and store it for an indefinite time somewhere underground. One of the problems here is, that even if the concentration of CO_2 in the atmosphere has risen by more than 50% since pre-industrial times,[26] the absolute amount of CO_2 in the atmosphere is still very low, presently about 410 parts per million. This means that roughly only one in every 2.500 molecules in air (consisting of nitrogen, oxygen, etc) is a CO_2 molecule. Filtering CO_2 out of the air, therefore, means that an enormous amount of air needs to be passed through any filter to remove a meaningful amount of CO_2. It is therefore that many technologies focus on capturing CO_2 at places where the concentration is higher, so-called point sources. These can be found at e.g. the exhaust of waste incinerators and thermal power plants. Next to that, also certain food producing plants using fermentation processes, such as breweries, and small scale (manure) digesters may serve as point sources of CO_2.

4.2 Carbon capture technologies

Carbon capture technologies are not new. The IEA[27] reports that in 2020 21 large scale carbon capture facilities are operating around the world with a capacity to capture 40 Mt CO_2 each year.[28,29] However, the implementation of carbon capture technologies lags behind compared to earlier estimations, especially because the price of CO_2 is in most places not high enough to warrant large scale investments.[27] Much of the captured CO_2 is used for enhanced oil recovery, where it is pumped into oil fields to pump up more crude oil. How contradictory this may seem, this is one of the technologies that actually makes carbon capture economical at the moment. The good thing of carbon capture technologies is that they can also be added to an already existing production facility that produces and emits a large amount of CO_2.

Once the CO_2 is captured, it can be compressed and transported by ship or pipeline. The captured carbon can be stored, to remove it from the atmosphere for an indefinite

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[26] https://www.climate.gov/sites/default/files/CO2_emissions_vs_concentrations_1751-2019_lrg.gif

[27] IEA (2020), CCUS in Clean Energy Transitions, IEA, Paris https://www.iea.org/reports/ccus-in-clean-energy-transitions, License: CC BY 4.0. The number refers to the installed capacity, it is not clear how much of this is actually used.

[28] 1 Mt is 1 Megatonnes, thus 1 billion kilogrammes (10^9 kg).

[29] This 40 Mt capturing capacity is actually only 0,1 % of the calculated total global yearly emission of 40 Gt CO_2 (https://essd.copernicus.org/articles/14/4811/2022/#section3).

timespan (Carbon Capture and Storage, CCS technologies), but it can also be used as feedstock for several chemical processes, to produce chemicals and materials. This is often referred to as Carbon Capture and Utilisation (CCU technologies).

Chemistry involving molecules with only one carbon atom, such as the CO_2 molecule, is often referred to as C_1 chemistry. Many chemical C_1 conversion processes are already well established on large industrial scale. They were developed decades ago to produce chemicals from (mostly) coal and natural gas (methane). Next to these chemical processes, CO_2 can also be used as feedstock for production processes on the basis of micro-organisms, so called microbial processes. The chemical as well as the microbial processes can be applied to produce small molecules, i.e. building blocks (see paragraph 2.2 and Figure 4.1) that can serve as monomers and thus be the precursor of man-made polymers and materials.

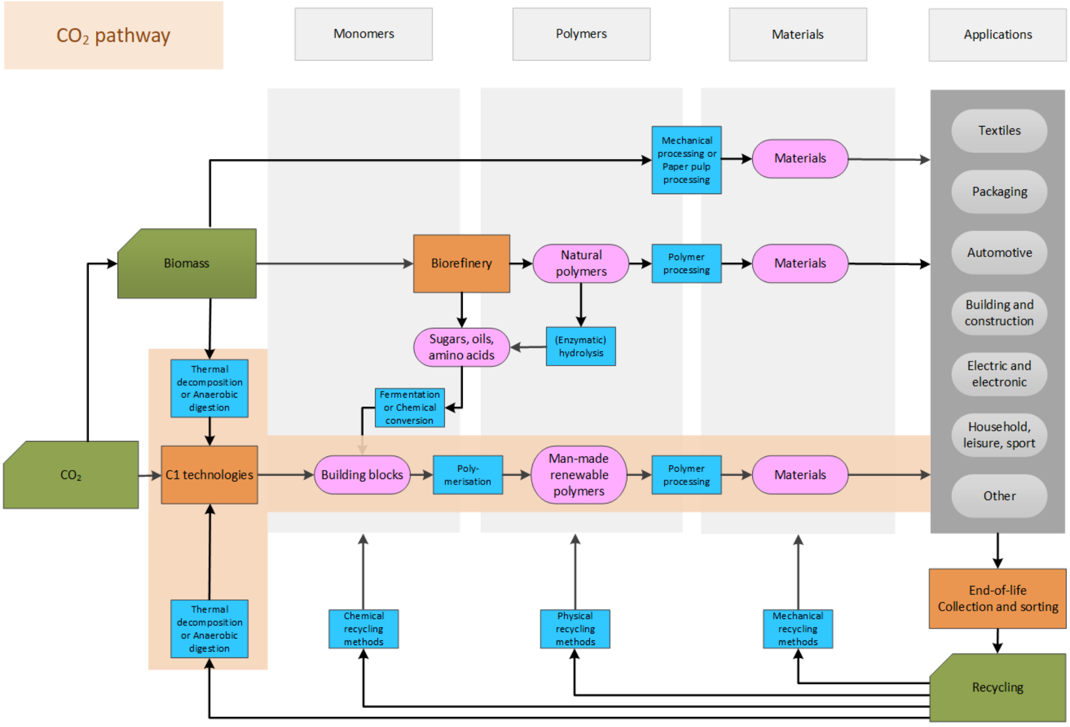

Figure 4.1. The renewable carbon-based system, highlighting (light orange) the CO_2 (CCU) pathway. (See Paragraph 2.6 for an explanation of the general structure of the scheme).

In the next paragraphs these processes and what they require are presented in more detail. The processes we describe in this chapter are *technology-based* approaches to capture carbon and produce chemicals (building blocks), man-made polymers and materials. As we have seen in the previous chapter, also living organisms produce polymers and materials starting from CO_2. In our line of reasoning, we refer to these processes as *nature-based solutions* to capture and use carbon for materials.

4.3 Chemical CO_2 conversion.

The first step in the conversion of CO_2 into other molecules can be the production of carbon monoxide (CO). CO is, in contrast to CO_2, a rather reactive molecule that can relatively easily be converted by current technology into other small molecules (see Figure 4.2).

The production of CO from CO_2 can be done in different ways. One approach is via the so-called *reverse water-gas shift (RWGS) reaction*, which forms CO (carbon monoxide) from CO_2 and hydrogen (H_2). This reaction is represented by the upper dotted line between CO_2 and CO in Figure 4.2. The reaction proceeds as follows:

$$CO_2 + H_2 \leftarrow\rightarrow CO + H_2O$$

It is an equilibrium reaction that can run in two directions, depending mainly on the temperature and the concentration of the reactants. Unfortunately, for the reaction to proceed to the right (i.e. towards CO production), high temperatures are needed[30] and as a result a lot of energy, which implies the reaction needs to be performed at large scale in order to be economically feasible. At lower temperatures the reaction to the left is favoured, called the *water gas shift* (WGS) reaction. This reaction is performed on large industrial scale, with the objective to produce H_2 from syngas (CO and H_2), which is produced by gasification of fossil feedstocks such as coal or natural gas. Currently, the reaction to the right producing CO from CO_2 is not performed at large scale, due to the unfavourable economics.

Another way to produce CO from CO_2 is via *electrochemistry*. Electrochemistry is being presented as a very promising new approach in the slipstream of the development of renewable electricity technologies. The essence of electrochemical processes is that electricity is directly used as the energy supplier (instead of high temperatures or H_2), and that also the electrons play an essential role in driving the chemical reactions. This

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[30] The reverse reaction becomes favourable at temperature roughly above 600 °C, https://en.wikipedia.org/wiki/Water-gas_shift_reaction.

reaction is represented by the second dotted line between CO_2 and CO in Figure 4.2. Most electrochemical processes are performed at relatively mild, frequently ambient, temperatures and pressures, which sets them apart from a technology such as the RWGS reaction. Preferably the reaction is performed in water. Together these aspects make electrochemistry often a potentially more sustainable option. Nevertheless, large scale production of CO through electrochemistry is not yet implemented, because it is still in an early stage of development.

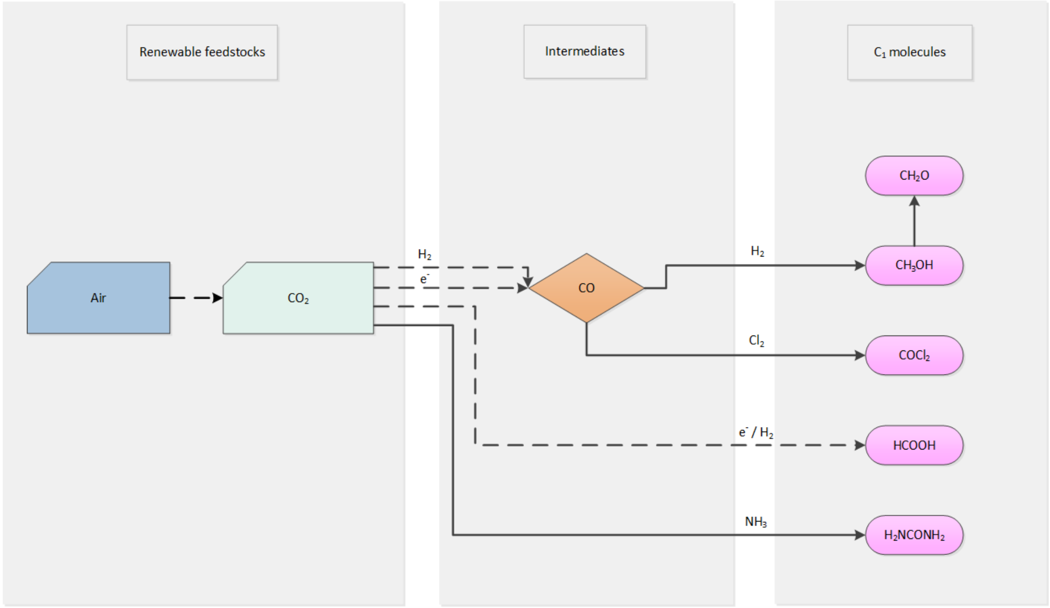

Figure 4.2. Possible pathways to produce reactive C_1 molecules starting from CO_2 directly or through CO as an intermediary. The dotted lines are processes that are not yet employed on large scale, the solid lines represent technologies implemented at large scale.

Once the CO is formed it can be converted into other small molecules by introduction of other reagents. For instance, methanol (CH_3OH) can be produced by reacting the CO with hydrogen (H_2) (see Figure 4.2). Methanol can subsequently be converted to formaldehyde (CH_2O).[31] Another example is phosgene ($COCl_2$) that can be produced by

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[31] Formaldehyde is a versatile molecule that is used in many applications., such as binders for strandboard, Mepal camping plates, but also as an embalming agent.

reaction with chlorine (Cl_2).[32] These small molecules still contain only one carbon atom, but they are rather reactive and can be used for the production of larger molecules that are building blocks for polymer production.

For some processes it is not necessary to first produce CO. For instance, urea (H_2NCONH_2) can be produced through a direct reaction between CO_2 and ammonia (NH_3).[33] Also formic acid (HCOOH) can be produced directly from CO_2. This reaction is another example for which an electrochemical process is being developed.
Many routes are thus possible, the molecules that are produced are however not yet building blocks, because they have only one reactive group. To produce materials additional conversion steps are necessary.

Figure 4.3 (on the next page) shows a wide range of possible pathways to convert reactive C_1 molecules into building blocks with more than one C atom, that can subsequently be used to produce polymers from these building blocks. The polymers presented here are materials that in principle can be recycled through chemical recycling (see the next chapter), but that we nowadays still make from fossil feedstocks (i.e. these are also examples of the so-called drop-in materials). The exceptions to this are PLA and PHA, which are produced from biomass, or biomass waste residue streams.[34]
Starting from the C_1 molecules these materials are industrially viable options, but other polymers, for instance those that are better biodegradable might also be developed (e.g. polyglycolic acid or PGA).

Next to the examples shown in Figure 4.2, many other small molecules can be produced by electrochemical conversion of CO_2, depending on the reaction conditions and the type of catalyst[35] applied, but these processes have generally not reached a larger scale.[36]

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[32] Phosgene is a highly poisonous chemical, that was used in World War I as a weapon, but it is also a versatile molecule, that is applied in controlled industrial setting for the production of polycarbonate and polyurethanes.

[33] Urea is well-known for its use as fertiliser in agriculture, but it is also a building block for melamine resin (MF), used for instance in Mepal camping plates and cups.

[34] PLA: polylactic acid, PS: polystyrene, PA66: nylon, PMMA: plexiglas, PET: polyester, PUs: polyurethanes, PC: polycarbonate, PHA: polyhydroxyalkanoate, PAs: polyamides.

[35] A catalyst is a substance that is added to a chemical reaction to increase the rate (speed) of the reaction, but is not consumed in the reaction. A specific catalyst may also influence the specific product that is formed in the reaction.

[36] According to Sun *et al.* (Chem 3, 560–587, October 12, 2017 © Elsevier Inc) CO_2 can be turned into 16 different products through electrochemistry, including: CO, oxalic acid ($H_2C_2O_4$), formic acid

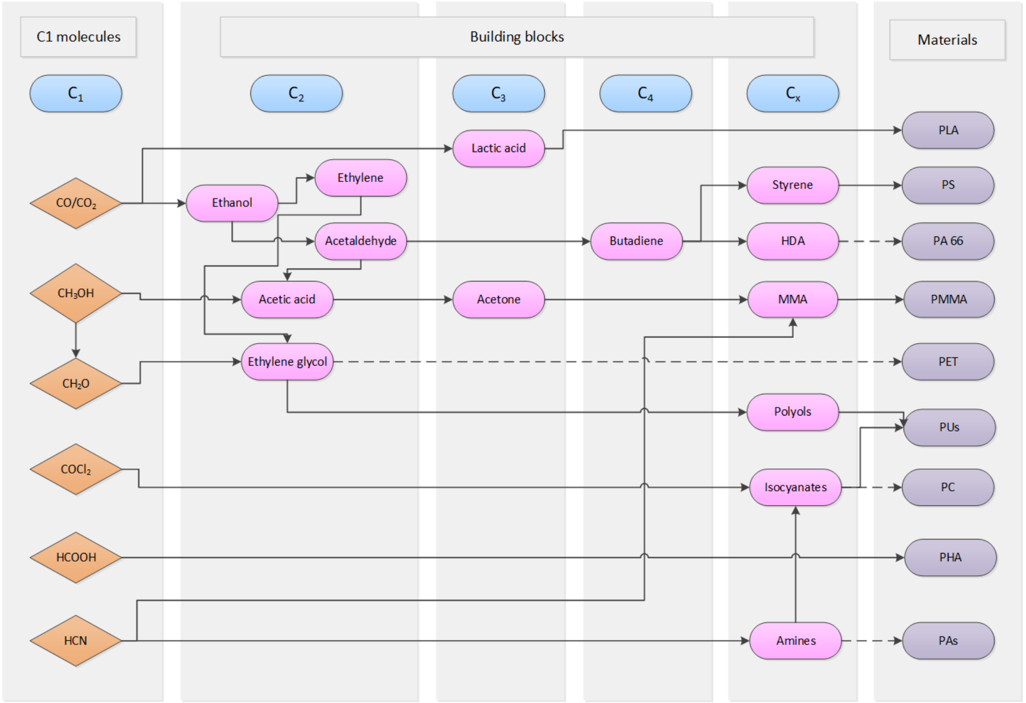

Figure 4.3. Possible pathways to produce building blocks with multiple C atoms that can be used to produce polymers, starting from various C_1 molecules. The polymers shown in this figure are materials we produce today mostly from fossil feedstock (apart from PLA and PHA) and that can potentially be recycled by chemical recycling methods back towards building blocks (see next Chapter). The dotted lines indicate that for that specific polymer the building block shown is only one of the two needed to produce the polymer. For the production of HCN; see section 4.5. See also footnote [34] on the previous page for explanation of the abbreviations.

Another, quite different process that can be applied to produce longer molecules directly from CO, is the so-called Fischer-Tropsch reaction. In this reaction CO, in combination with hydrogen, is converted to longer molecules that only contain carbon and hydrogen

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(HCOOH), formaldehyde (HCHO), methanol (CH_3OH), methane (CH_4), ethylene (C_2H_4), ethanol (C_2H_5OH), ethane (C_2H_6), and n-propanol (C_3H_7OH).

atoms, and therefore strongly resemble the present fossil feedstocks. This reaction can roughly be depicted as follows:

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$$

This reaction scheme shows that in principle it is possible to produce much used polymers like PE[37] through this pathway. The Fisher-Tropsch process is presently performed at many industrial sites all over the world, especially to produce liquid fuels, starting from a variety of (mostly fossil) feedstocks, but as far as we know, nowhere starting directly from CO_2.

From the reaction scheme it is also clear that for each molecule of CO about two molecules of hydrogen (H_2) are needed. A high demand of hydrogen for the follow-up reactions when starting from CO_2 is not only the case for the Fischer-Tropsch reaction but also for most of the other reactions shown in Figure 4.2. The introduction of CO_2 conversion technologies as an alternative for fossil-based feedstocks, therefore also requires the production of renewable hydrogen (as was already introduced in Figure 1.2)

4.4 Microbial CO_2 conversion processes

Next to all the chemical processes presented in the previous paragraph, CO_2 can also be converted into other small molecules by using microbial processes. In microbial processes algae, cyanobacteria, bacteria or yeasts are applied to drive the reactions.

The decisive difference between these categories is that algae and cyanobacteria contain chlorophyll, therefore they have the ability to use sunlight as the energy source for their metabolism (Figure 4.4). Bacteria and yeasts normally need another external energy source, such as sugars or fats, just like we do. These sources can be found in biomass or biomass side-streams, but will then need to be produced first (by crops). Within the framework of this booklet the application of these bacteria and yeasts to produce building blocks therefore ranges under the biomass pathway (see paragraph 3.5.2). Applying algae or cyanobacteria without the necessity to feed them with biomass ranges under the CO_2 pathway. The same counts for (genetically modified) bacteria or yeasts that can use H_2 or even light as energy source, or some specific bacteria, such as the purple bacteria, that can use light as energy source.

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[37] Polyethylene, for which the n in the equation above can range typically range from 4.500 to 35.000 for different material grades.

The advantage of applying microbial approaches is that micro-organisms can directly produce larger molecules from C_1 chemicals,[38] in contrast to the chemical routes where every step needs to be performed separately. In many cases these molecules become part of the micro-organisms structure, or are stored for later energy supply. To be useful as feedstock for materials, the molecules need to be extracted from the microbial biomass. There are, however, also cases where the micro-organisms make molecules which they excrete, so they may be harvested more easily. An example are certain cyanobacteria that can produce lactic acid (the building block for PLA) which they excrete.

Figure 4.4. Algae range among the micro-organisms that can produce interesting chemical compounds from CO_2 using light as energy source.

A recent approach to develop faster microbial conversion processes is by the use of *gas fermentation*, where CO_2 or CO, together with renewable hydrogen are converted to small molecules by microorganisms. Although various pathways to molecules are currently being explored, including the production of C_2 to C_4 acids and alcohols,[39]

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[38] In their metabolism this is done in consecutive steps, for instance the Calvin cycle, which produces three-carbon sugar phosphate molecules in three steps. However, when watching from the outside, the resulting three carbon containing molecule is the product of the microbial conversion.

[39] C_2 to C_4 acids and alcohols are acids or alcohols with 2, 3 or 4 carbons. Ethanol; C_2H_5OH is thus a C_2 alcohol.

currently the only process operated on industrial scale is the conversion of CO to ethanol.[40] Also for these processes (renewable) hydrogen is needed. A bottleneck is that hydrogen, just like most gases, dissolves poorly in water. To increase the solubility, the processes can be performed at higher pressure, but another option is to first produce formic acid from CO_2 (through electrochemistry, see the previous section) and then use this as feedstock for the micro-organisms. (See also footnote[19])

However, to produce a meaningful amount of chemicals in this way takes time and thus money, which is one of the challenges of the development of these production routes. Another common challenge is how to separate the produced molecule from the reaction medium, which is often referred to as downstream processing (often referred to as DSP). These processes are considered expensive processing steps.

4.5 Point sources for C_1 conversion processes

In this chapter we presented many technological pathways to produce building blocks and subsequently materials starting from CO_2. What the technologies have in common is that they all start from a molecule that contains only one carbon atom and stepwise build more complex molecules containing more carbon, until finally a polymer is produced.

As discussed in paragraph 4.1 the capture of CO_2, either from the air or from a point source can be considered as a first step in these production pathways. Especially the point sources form a very diverse set of options, which we will explore in more depth in this paragraph.

One of the point sources that we already introduced in paragraph 4.1 is biomass. This could be either a side stream of a biomass based process, e.g. CO_2 from a fermentation process, such as beer brewing, or a result of the processing of a biomass residue. One such example is the anaerobic digestion of manure and other biomass left-overs. This process produces biogas, which is a mixture of CO_2 and CH_4. We already know that CO_2 is an interesting feedstock molecule, however this also counts for CH_4, methane. Just as with CO_2, also from methane other small molecules can be made, partly with existing technologies. Methane can be converted into syngas, and can then be used to produce various C_1 molecules as is shown in Figure 4.5. The approach based on methane can be

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[40] Lanzatech's microbial gas fermentation process provides routes to ethanol, jet fuel and high-value chemicals from gas streams including industrial off-gases from e.g. steel and alloy mills; syngas generated from any biomass resource (e.g. municipal solid waste (MSW), organic industrial waste, agricultural waste); and reformed biogas. (www.lanzatech.com).

an important additional process for the so-called total-use principle of biomass (i.e. try to use all components of a crop for an application with a value as high as possible). Wet, partially degraded or otherwise unusable fractions of biomass can thus be put to use as feedstock for C_1 conversion technologies.
A similar reasoning applies to other types of waste. Waste-water treatment sludge, for instance, can also be used as feedstock for anaerobic digestion, producing again CO_2 and CH_4. And the incineration of municipal solid waste or other waste fractions can produce CO_2, or syngas (CO and H_2) if a gasification process is applied, which can be recovered and serve as feedstock as depicted in Figure 4.5.

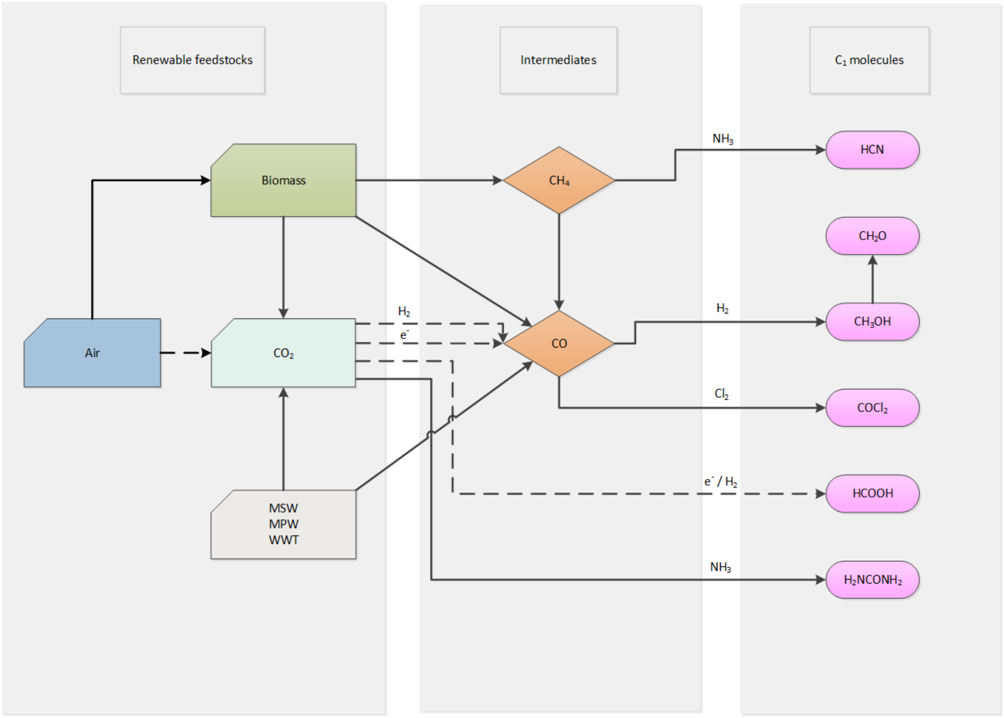

Figure 4.5. Technology based routes to produce C_1 molecules can not only start from CO_2 capture from air, but also from anaerobic digestion of biomass (which produces CO_2 and CH_4), from burning or gasification of biomass (to CO_2 or CO) from burning or gasification of MSW (Municipal Solid Waste), MPW (Mixed Plastic Waste) or from anaerobic digestion of WWT (sludge from Waste Water Treatment) or other point sources not mentioned in this figure.

A general approach to this could be a kind of cascading for waste valorisation:

1. Wet, biomass containing waste can be digested to produce biogas, CO_2 and CH_4, as feedstock for C_1 technologies.
2. The watery side streams of this process contain minerals and nutrients that can be recycled in a meaningful way, e.g. as fertilizers
3. The solid left-overs can be dried and together with other solid and/or contaminated waste be incinerated to CO_2, that can be recovered and serve as feedstock for C_1 technologies and some remaining ash.

In this way a localised production of feedstocks for C_1 technologies could be implemented.

4.6 Conclusions

A large variety of technologies that can potentially play a role in the introduction of the CO_2 pathway was introduced in this chapter.

Comparing the various processes to convert CO_2, an important difference is that with the chemical and electrochemical processes, in the first step very small molecules containing only one carbon atom are made, which require additional reaction steps to convert them into more complex building blocks that can be meaningfully applied for the production of carbon-based materials.

The microbial production routes offer the possibility to obtain more complex, multi carbon molecules in high selectivity, in a single process step. However, the time required to produce meaningful amounts of these molecules is generally long. Nevertheless, this approach may be attractive for the production of molecules that are more challenging to make efficiently via chemical or electrochemical reactions. Further development of microbial CO_2 conversion technologies, which do not require biomass as feedstock, is necessary to bring it to large-scale industrial implementation.

Transitioning to renewable C_1 feedstocks such as CO_2 or biogas will require further innovation and investments in feedstock preparation and purification, as well as in implementation of renewable energy in these conversion processes. Furthermore, the presence of renewable hydrogen is a requirement for these processes. The conversion of C_1 chemicals to more complex molecules requires additional energy with every step, and hence will add to the overall costs. Selectivity towards the desired type of molecule is therefore key in order to minimise the use of energy, and the co-production of waste, and this is still the subject of many research and development trajectories.

5 The recycling pathway, recycled materials as feedstock

5.1 Introduction

Once the materials that were discussed in the previous paragraphs have been used in a product and the product has reached the end of its life, they can serve as feedstock for new materials. This can be done in many ways, depending, among others, on the kind of product and the exact composition of the materials it is made of.

Recycling of materials back into a similar product is already done for many materials such as glass, paper, metals, plastics and to a lesser extent textiles. The first step of recycling is always collection of the used products. Depending on the material and the country, different collection systems are in place. For instance, in the Netherlands waste paper and cardboard (called old paper) is collected from households and companies. For plastic packaging, in many countries, especially in the EU, also separate collection is in place, partly through a deposit refund system (mostly for bottles), partly through a special collection bin or bag. For proper recycling into high value products, separate collection and subsequent sorting is of the utmost importance. The cleaner the waste stream and the less different types of material present, the easier the production of the new product will be, irrespective of the exact recycling technology used. Mixing of different types of plastics into a new recycled plastic generally leads to inferior properties: low(er) strength, brittle, turbid, etc. A serious problem is posed by the present use of multi-materials in products: multilayer plastics, textiles consisting of a mixture of fibre types, etc. Whereas these materials may exhibit very good properties, recycling them is extremely complicated, because separation of the materials is next to impossible, even if they are well collected and sorted. Design for recycling strategies will need to be implemented to tackle this problem at the source.

There is some ambiguity in the terminology used for different recycling methods in the different areas. For this booklet we follow the terminology recently proposed by Harmsen et al.[41], because this fits well with the approach that forms the basis of this booklet, based on the build-up of all carbon-based polymeric materials (Chapter 2).

Following this terminology we can distinguish four fundamentally different ways of recycling, presented in Figure 5.1:

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[41] Harmsen, Paulien, Michiel Scheffer, and Harriette Bos. 2021. "Textiles for Circular Fashion: The Logic behind Recycling Options." *Sustainability* 13, no. 17: 9714. https://doi.org/10.3390/su13179714

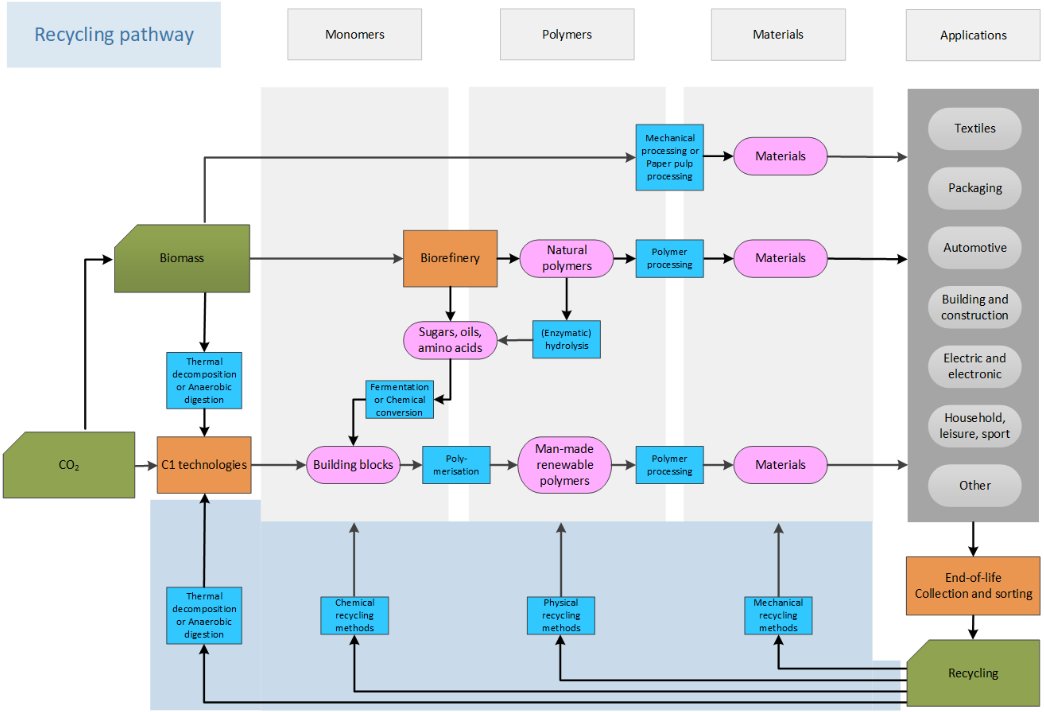

Figure 5.1. The renewable carbon-based system, highlighting the four different recycling pathways. (See Paragraph 2.6 for an explanation of the general structure of the scheme).

- Through mechanical methods, in which the basic 3D structure of the materials stays intact, but the product is newly shaped, this is often applied for fibrous structures such as paper and textiles.
- Through physical methods, in which the 3D structure is lost and the materials are reshaped into new 3D structures by physical methods (melting or dissolving). An important example is the widely applied recycling of plastic packaging (which is in the plastics industry often referred to as mechanical recycling, see section 5.3).
- Through chemical methods, in which the polymeric structure is broken down, back to the building blocks (or even precursors, smaller molecules preceding new building blocks), and the building blocks are repolymerized into new polymers and subsequently formed into new 3D structures.
- Through thermal decomposition or digestion, where the materials are incinerated or optionally anaerobically digested if they are biodegradable. The

materials are broken down all the way back to CO_2 (and methane in the case of digestion) and these can be used as point sources for applying the C_1 technologies discussed in Chapter 4.

The next paragraphs will elaborate on each of the four methods.

5.2 Mechanical recycling methods

The first steps of mechanical recycling methods are obviously collection and sorting. The cleaner the input streams, the less recycled input needs to be discarded and the higher the quality of the recycled products. After sorting, depending on the material type, a number of methods are used to make a new product from the recycled stream (see Figure 5.2, highlighted in blue)

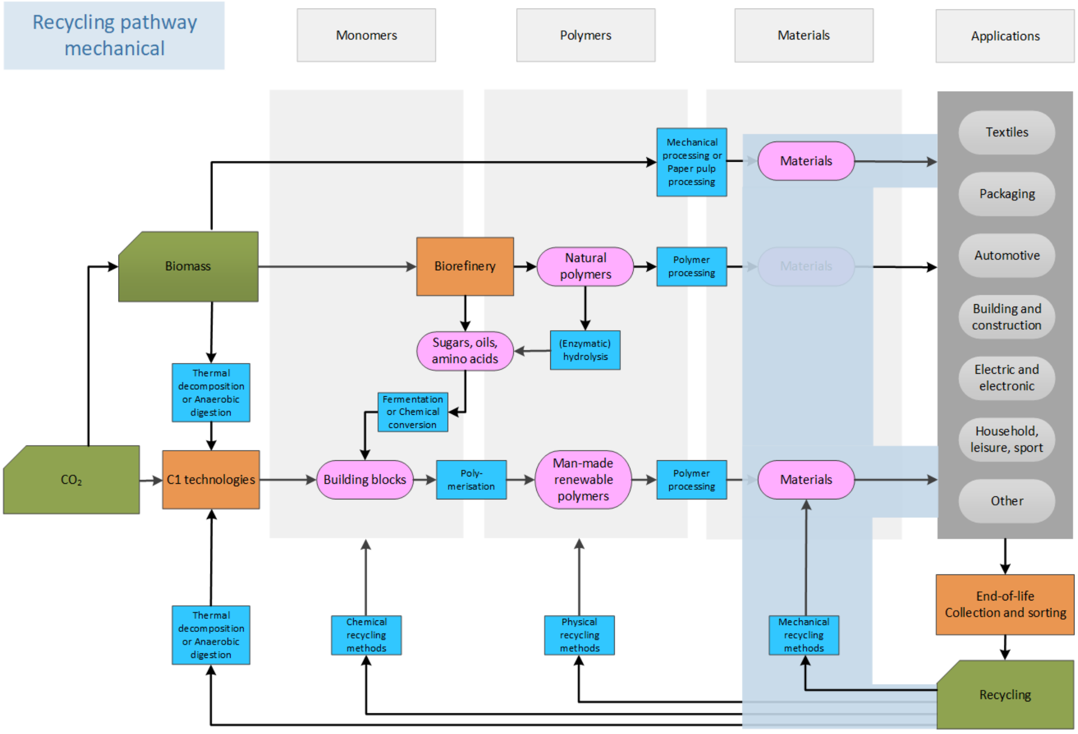

Figure 5.2. The renewable carbon-based system, mechanical recycling methods (light blue), keeping the basic 3D structure of the materials intact.

The paper recycling process has already been in place in the Netherlands for decades. Waste paper is collected and transported to dedicated recycling plants, where it is cleaned and subsequently dispersed in water to paper pulp, just as is done in the case the paper is produced from virgin[42] pulp. The pulp is distributed over a broad mesh, where it is dewatered, and the pulp forms a paper once more. Paper fibres are generally said to be recyclable 7 times, after which their fibre length has reduced too much to be used once more. In the recycling process, usually a small fraction of virgin pulp is added to improve the properties. Due to this effective recycling system in place, the demand for new feedstocks is drastically reduced. However, recycled paper is often contaminated with inks, glues and other substances, which means that recycled paper cannot be used safely in food contact applications, such as food packaging.

Also a small part of textiles are recycled through mechanical methods. Mechanical recycling is applied generally for high value textiles, that consist of yarn with long fibres. Knitted wool, for instance, has been recycled since ancient times by simply drawing out the knitting and then knitting a new garment from the yarn.

These days textile recycling through mechanical methods mostly implies that first the fabric and subsequently the yarn are disintegrated, and the original fibres are separated by methods such as cutting, tearing, shredding and carding. Applying these processes implies that the 3D structure of the fibres remains mostly intact, and these fibres are subsequently respun into a new, recycled yarn, which can then be used to produce a new fabric.[43] However, because mechanical methods generally break down the original yarn, they also may result in fibre length reduction, which causes quality loss. A small amount of long virgin fibres may be blended in when the new yarns are produced, and this may help to improve the general strength of the recycled yarn. Nevertheless, the shorter fibre length in fabrics from recycled yarn generally means that they wear out more quickly than fabrics from virgin yarn. Therefore, mechanically recycled fibres often end up not as a fabric, but as a non-woven, and are then used for instance for upholstery or for insulation applications. Cotton and wool are examples of fibres that are mechanically recycled nowadays.

Another example of a mechanical recycling method is the shredding of wood waste into small particles that can be used to produce particle boards. This is done generally at wood processing plants, but can also in principle be applied to wood waste from other sources. As with the other mechanical methods it is important that the waste stream is

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[42] The term virgin feedstock or virgin material is generally used to indicate a material or feedstock that is produced from the original (non-recycled) raw materials.

[43] More background information on the recycling of textiles can be found in the Groene Grondstoffen publication: Textiles for Circular Fashion, Part 1: Fibre Resources and Recycling Options, Paulien Harmsen and Harriëtte Bos.

clean. At a wood processing plant this is obviously no issue. End-of-life wood products, however, often are painted or laminated, which makes this kind of mechanical recycling methods less applicable.

5.3 Physical recycling methods

Physical recycling methods use physical processes to make fibres or polymers suitable for reprocessing, which means either melting or dissolving them. With physical recycling the 3D structure of the material is changed, but the polymeric molecules that make up the materials remain largely intact (Figure 5.3). After melting or dissolving, the standard polymer processing methods are available to produce a new 3D product.[44]

In the world of plastics, physical recycling methods are applied broadly, but they are often referred to as mechanical recycling. Especially packaging material, which forms

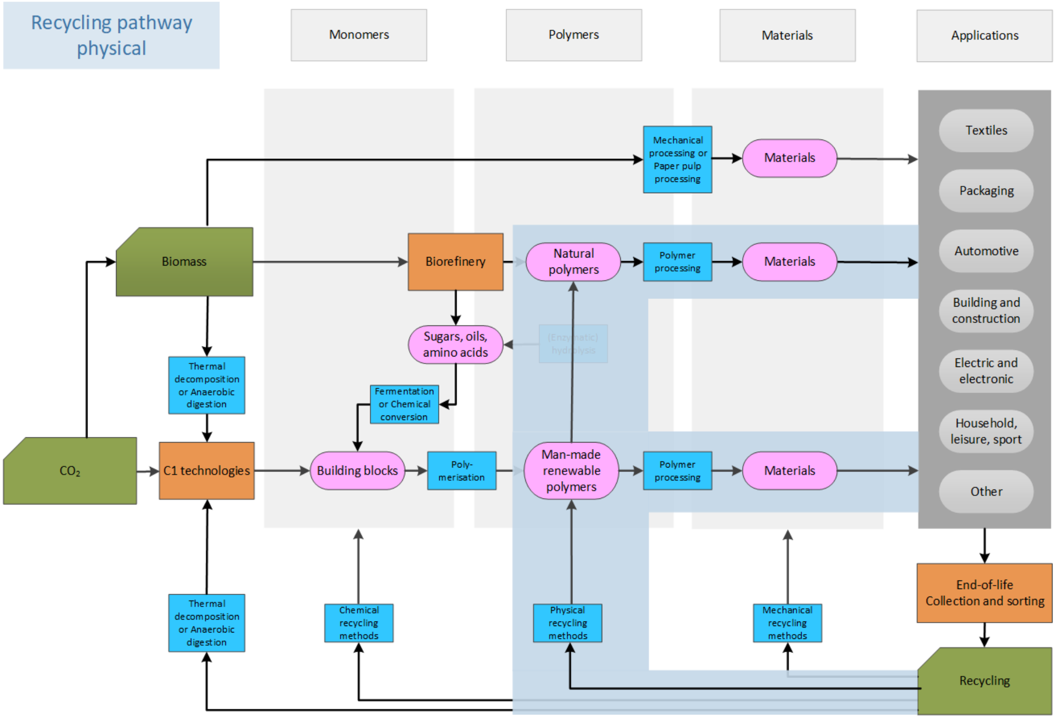

Figure 5.3. The renewable carbon-based system, physical recycling methods (light blue), keeping the polymeric structure intact.

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[44] See Chapter 2.4 for a brief overview of polymer processing techniques.

approximately 40% of the total application of plastics, is recycled through physical recycling methods. But also other plastic products are recycled in this way, for instance building and construction materials such as PVC piping.

Figure 5.4. Packaging waste often contains a large fraction of mixed plastics of different colours.

After collection, the materials need to be sorted with respect to polymer type; this is generally done via optical sorting by means of near infrared technology. After that, they are generally shredded into smaller parts and washed. Some polymers float (like PE and PP) and some sink (like PET), so for better separation a float-sink separation is often applied. After drying, the parts are fed to an extruder, where they are melted, eventually mixed with additives and then upon leaving the extruder cut into uniform pellets or granulate. The granulate can be used to produce new products, for instance through injection moulding, film blowing or other standard polymer processing techniques. Because it is difficult to meticulously sort the waste plastics, and because plastics generally deteriorate slightly during use and processing, recycled products from these methods often have somewhat inferior properties compared to a virgin plastics product. Also, the mixing of recycled fractions of a spectrum of different colours (see Figure 5.4) leads to the necessity to give recycled products a dark colour (mixing various colours often leads to an unattractive brownish, greyish colour). By means of colour sorting or mixing the recycled material with virgin plastic, these effects can be mitigated.

Another important challenge in relation to recycling of plastic packaging waste, is that the exact composition of the recycled material is unknown, so real circular use for food-grade packaging is a challenge due to safety restrictions. The combination of design for recycling and dedicated collection, for instance of transparent bottles as is done with PET, gives much more possibilities to make high value recycled materials, which can in some cases even be applied in food-contact products. Transparent plastics can be reprocessed into new transparent products, and especially PET offers the possibility to repair the (molecular) damage that was done during the use phase, by a process called solid state post condensation. In this way the mechanical properties are restored almost up to the properties of virgin PET materials. In practice, the recycled PET bottles are not necessarily processed into new bottles but more into textile fibres/yarns, which are then branded as produced from recycled materials. However, in Western Europe, due to the implementation of stricter circularity regulation, most recycled PET from bottles goes back into bottles these days.

A methodology that is also based on physical recycling principles, but takes a different approach, is dissolution. In this process the polymer is dissolved in a tailor-made organic solvent after which impurities can be removed and the plastic is precipitated to be reused. Several processes have been developed over the past years. Two examples are the CreaSolve® process,[45], used to recycle expanded polystyrene (Tempex)[46], and the Vinyloop® process, which has been running for over a decade to recycle PVC cables.[47] These dissolution processes are generally able to produce recycled polymers of good quality, at a much lower CO_2 footprint and energy demand than virgin materials, when they succeed in recapturing a high percentage of the solvents used.[45]

For textiles, physical recycling methods are also an option, depending on the type of polymer that the textile is produced of. Polyester textile fibres (which is the same

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[45] https://www.creacycle.de/en/the-process In some studies the CreaSolve® Process is classified as chemolysis i.e. a chemical recycling process, which it is not: https://renewable-carbon.eu/news/the-creasolv-process-is-neither-a-solvolysis-nor-chemical-recycling/, in the process the polymers are not broken down but stay intact. See also footnote [48].

[46] This initiative went bankrupt early 2022, due to due to, among other things, increasing energy prices and a shortage in supply of used insulation foam. https://www.recyclingmagazine.nl/algemeen/piepschuimrecycler-polystyrene-loop-failliet/47545/, combined with low prices of virgin feedstock.

[47] The process was used to separate PVC from a mixed waste stream, but it could not remove low molecular weight phthalate plasticizers during recycling, tightening EU regulations meant the plant in Ferrara (It) that applied this technology was closed down in 2018. https://en.wikipedia.org/wiki/VinyLoop

material as the PET used in bottles) can be respun into a filament fibre. If a fabric is composed solely of polyester, small pieces of the fabric could possibly be fed to an extruder to be molten, and respun, it would not be necessary to decompose the fabric down to the yarn and subsequently the fibre. The dyes and other additives present in almost all textiles, however, will make recycling into an appealing new fibre, yarn and subsequently fabric difficult. Nevertheless, a number of industrial parties is involved in developing these kind of processes.[43]

Another example of textile recycling by physical methods is the recycling of cotton or cellulose-based fibres to create a regenerated cellulose fibre (viscose, see also section 3.4) by dissolving the cellulose in a solvent, followed by solution spinning. This is the pathway back through natural polymers as depicted in Figure 5.3.

Figure 5.5. Post-consumer textiles need to be meticulously sorted and separated in order to be meaningfully recycled through physical recycling processes.

A particular difficulty with recycling textile fibres in this way is the fact that most modern textile yarns are composed of more than one different types of fibres with different optimal recycling options. Take for instance the much-used cotton-polyester blend; the polyester might be recycled by melting and spinning, the cotton by applying the viscose process, thus dissolving and spinning, but for the mixture application of these processes is not possible, unless the fibres are completely pre-separated into the two fractions (Figure 5.5). Application of chemical recycling methods might be more promising (see next paragraph). Another spoilsport for these kinds of processes is the presence of elastane in many garments. Even if elastane generally is present in only a very small percentage, it inhibits meaningful application of the physical recycling processes.

5.4 Chemical recycling methods

Chemical recycling methods use chemical processes to break down the materials, which means that the polymers that make up the 3D materials are broken down (chemical bonds are broken), sometimes as far down as to their original building blocks or beyond. This can be done by chemical methods (then called chemolysis)[48], biological methods (e.g. with enzymes), or also with thermo-chemical methods (called thermolysis). After chemical recycling, the building blocks can be used to build-up (polymerise) a new virgin

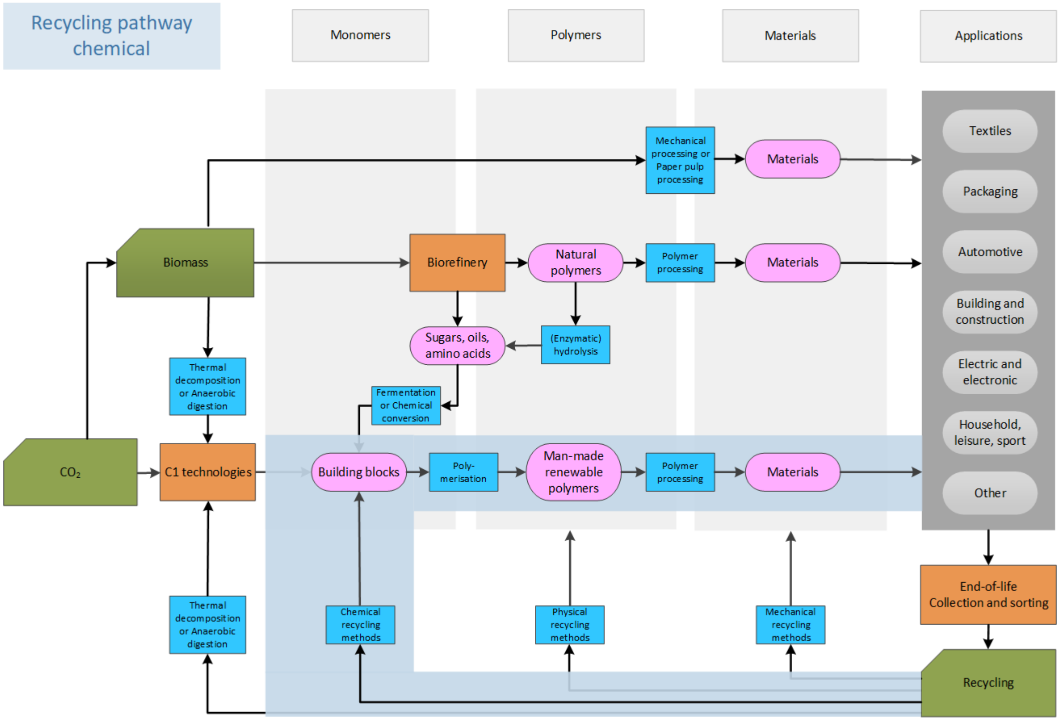

Figure 5.6. The renewable carbon-based system, chemical recycling methods (light blue), breaking down the polymers, while keeping the building blocks intact.

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[48] The suffix -lysis comes from the Greek verb λυειν, which means loosening something from something else. Chemolysis can thus be freely translated as breaking up something using chemical methods.

polymer again, which can then be reshaped into a 3D material structure. (See Figure 5.6)

5.4.1 Chemolysis

Chemical recycling methods through chemolysis are well suited for polyester fibres. During chemical recycling of polyester (part of) the ester linkages are broken down by chemical means or by enzymes. The larger the remaining building blocks, the lower the subsequent processing costs are. The fact that the polymeric molecules are broken down into small fragments gives the great advantage that removal of contaminants and dyes is much easier because the smaller fragments can be cleaned in solution. In addition, the building blocks (monomers) can be purified using common techniques like filtering, recrystallisation or distillation. After removal of the impurities, the polyester monomers can be repolymerised towards their original state and properties. In this way it is thus possible to make materials that have the same properties as virgin materials, which is a huge advantage compared to the other recycling methods.[43]

For other polyester products next to fibres, such as bottles or packaging blisters, the same kind of technology can be applied, which leads to similar advantages. Proper sorting and separation of the waste stream is a prerequisite for the application of these kind of technologies.

Chemical recycling methods are also well suited for nylons. In the process all of the amide bonds which form the backbone of the nylon polymer are broken down by chemical means or by enzymes. Nylon 6, for instance, is depolymerised to retrieve its original building block caprolactam. DSM states that this process is not more expensive than the production of virgin caprolactam, and it is much more environmentally benign.[49]

PET can be fully depolymerised into its building blocks, but there are also processes under development in which the PET is only partly depolymerised.

Another recent development is the chemical recycling of polyurethane mattresses and other urethane products following the same technological principles.[50]

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[49] Buijs, W. (2020). https://www.duurzaammbo.nl/images/pdf/Presention%20DSM%20Nylon-6%20Recycling%20C2C%20Desso_WB.pdf

[50] Kemona A, Piotrowska M. Polyurethane Recycling and Disposal: Methods and Prospects. Polymers (Basel). 2020 Aug 5;12(8):1752. doi: 10.3390/polym12081752. PMID: 32764494; PMCID: PMC7464512.

As explained above, chemical recycling by depolymerisation of the polymer chains back into building blocks has the great advantage that pure and purified building blocks can be produced from which new polymers with the same properties as the virgin materials can be made. However, this technology is only applicable if the polymerisation reaction that forms the polymer is reversible, so that the links between the building blocks can be broken in a controlled way. The type of polymers where this is possible selectively and efficiently are called condensation polymers. However, there are many polymers, the so-called addition polymers, for which the polymerisation reaction is not reversible, and selective depolymerisation into the original building blocks is not possible. The addition polymers comprise well known materials such as PE, PP, PVC, PS (for the abbreviations see footnote[34]) and many rubbers. For recycling of these polymers also the term chemical recycling is used, but in this case the processes are very different and fall under the category thermolysis.

5.4.2 Thermolysis

Thermolysis processes are often less specific than the chemolysis processes, typically scission of bonds at random positions in the polymer chain occur. This means that the polymers generally are not converted back into their original building blocks, but into a mixture of different small molecules, that may be building blocks for the original polymer, for another polymer or may not be a building block at all, because they do not have the sufficient amount or type of reactive groups (see Chapter 2.2).

Often thermolysis processes are applied to produce fuels from waste plastics, but in our search for renewable carbon for materials this is not a fruitful route. Pyrolysis (also referred to as thermal cracking) and gasification are two main thermolysis processes that are presently applied to produce new feedstocks for carbon-based materials.[51] The advantage of thermolysis processes is that the feedstock can be a mixed fraction of (plastic) waste. Nevertheless, this fraction should not oxygen, chlorine or nitrogen, so mixtures of for example polyethylene and polypropylene are acceptable, but broader mixtures of plastic waste will need sorting or additional pre-processing. Also for thermolysis processes, better sorting and separation of the waste fraction leads to less losses and energy use in the process.

Gasification is an energy intensive process. It is performed at high temperatures (higher than 700 °C) and during the process some oxygen is added. Gasification produces syngas (CO and H_2), which can serve as input for CO/CO_2 conversion technologies as described in Chapter 4.

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[51] More background information can be found in: Eunomia, Chemical recycling: State of Play. https://www.eunomia.co.uk/reports-tools/final-report-chemical-recycling-state-of-play/

Pyrolysis is also an energy intensive process. It is performed at high temperatures (but lower than gasification, typically above 400 °C) in the absence of oxygen. Pyrolysis produces pyrolysis oil (and char and gaseous by-products). Pyrolysis oil is a mixture of different hydrocarbons, and, when the feedstock contained oxygen, also different organic acids are produced. Pyrolysis oil can serve as feedstock for naphtha cracking[52], but only after purification (which is energy intensive). Also the ratio of pyrolysis oil to naphtha in the feedstock needs to be kept low, because contamination of the feedstock reduces the efficiency of the process. It is therefore assumed that it is likely that the process cannot run independently of the production of virgin (fossil based) building blocks.[51] There are still many uncertainties about the efficiency of this process, but it is definitely energy intensive and produces not one building block but a mixture of monomer building blocks, that each need to find a destination to make the process economically viable. The process is nevertheless developed further, because it gives the (petro-)chemical industry the possibility to keep using the cracker infrastructure that they have operated for many decades.

As described in Paragraph 3.5.2, BioBTX employs a special catalytic pyrolysis process, that produces (a mixture of) aromatic building blocks, that can, next to biomass, also use waste plastics as input. Other high temperature processes are also being developed by several parties, but it goes beyond the scope of this booklet to elaborate further on this topic.

5.5 Thermal recycling methods

When all above-described methods fail because the material is too contaminated, too deteriorated, or otherwise unfit, the most drastic method is to incinerate or anaerobically digest[53] the materials. These processes produce (useable) heat. Even though formally these processes are not seen as recycling, during incineration CO_2 is formed, and during anaerobic digestion CO_2 and also CH_4, which can be captured and used as input for the C_1 technologies described in Chapter 4. (See Figure 5.7).

Furthermore, controlled incineration or digestion combined with CCU prevents uncontrolled emission of greenhouse gases into the atmosphere by e.g. rotting processes, and it may also prevent the accumulation of persistent materials in the environment like the infamous plastic soup.

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[52] Naphtha cracking is the process that produces (oxygen free) chemical building blocks such as ethylene and propylene from fossil oil. It is done at large scale and is energy intensive.

[53] Only in the case the material is biodegradable.

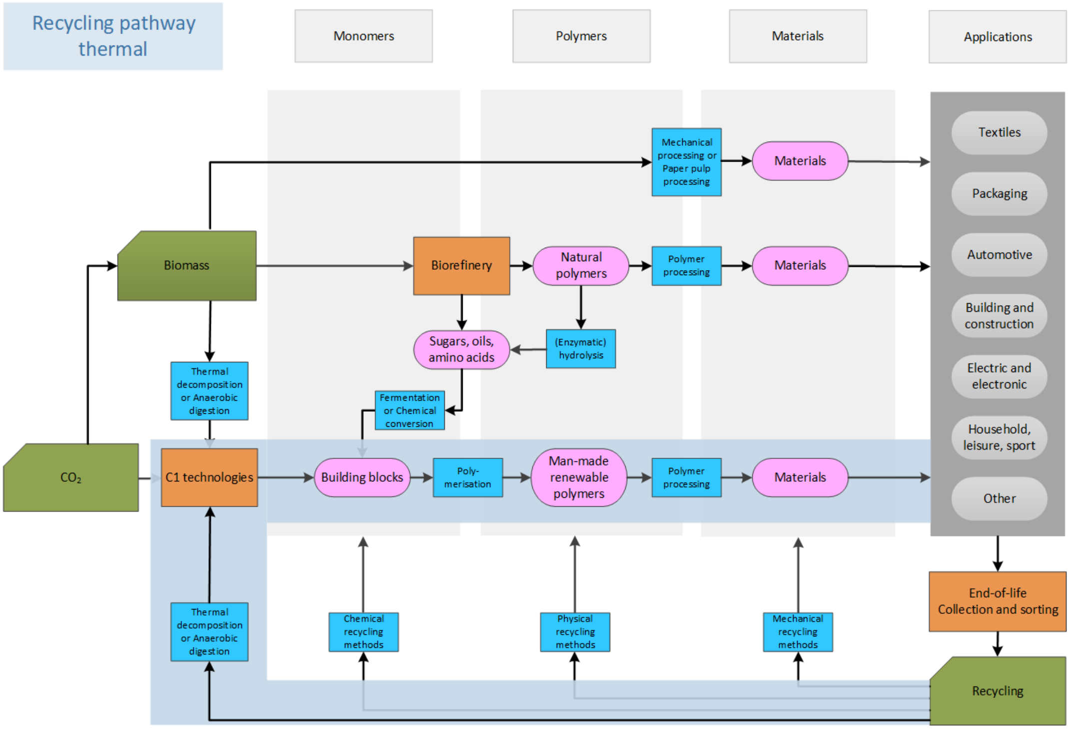

Figure 5.7. The renewable carbon-based system, thermal recycling methods, or anaerobic digestion (light blue), all the way back to CO_2 or other C_1 molecules.

5.6 The importance of circularity for carbon-based materials

Circular use of carbon-based materials by applying recycling technologies to produce new feedstocks is important to lower our dependence on virgin feedstocks. However, from the previous paragraphs it is clear that any combination of recycling is never going to fulfil all our feedstock demand, even if world-wide need for carbon-based materials would remain at the same level as it is now or would diminish. Recycling comes with the inevitable loss of a significant amount of the original material, and that is not counting the material that is leaking out of the materials system due to wear and tear (the microplastics), bad discarding behaviour, process losses, or for other reasons. New feedstocks will always be needed, but in the post-fossil era this feedstock needs to come from renewable (biogenic) carbon, i.e. CO_2 or biomass as we discussed in Chapter 3 and 4.

Nevertheless, recycling of materials can provide a significant contribution to our future materials need, but for recycled materials to be sustainable several criteria are important. Stretching the three key elements of "the new plastic economy" as described by the Ellen MacArthur Foundation to carbon-based materials in general; we need to make sure that:[54]

1. All carbon-based materials are used circularly (repurposed) as much as possible in applications of equal value
2. Leakage of carbon-based materials into the environment is avoided
3. The production of virgin carbon-based is renewably sourced

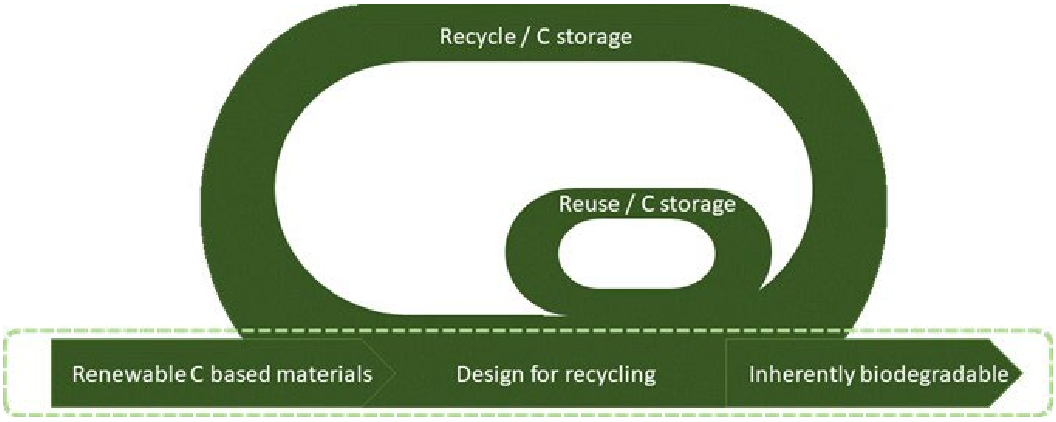

Figure 5.8. The key elements of future materials use. Abstracted version from the 'new plastics economy', made relevant for all carbon-based materials. After the Ellen MacArthur Foundation.

In Figure 5.8 an abstracted version of the EllenMcArthur Foundation approach is shown. Apart from the three key elements mentioned above, also the implementation of design for recycling principles for all carbon-based materials is essential. The longer we can keep the materials in the loop, the less (virgin) feedstocks we need. However, carbon-based polymers deteriorate in time, due to use, exposure to light or heat, wear and tear, absorption of contaminants, etc., their properties diminish and reuse is not endlessly possible. Mechanical and physical recycling methods, as presented in Chapter 5.2 and 5.3, have their limitations, materials cannot be endlessly recycled in this way, and generally the properties of recycled materials are not as good as of virgin materials.

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[54] https://ellenmacarthurfoundation.org/the-new-plastics-economy-rethinking-the-future-of-plastics.

Figure 5.9: Bits of non-degradable plastic waste inevitably leak into the environment and pose an ever increasing environmental problem. (Photo: Harriëtte Bos)

Chemical recycling can in some cases produce new materials that match the properties of virgin materials, but also in these recycling processes there is a significant fraction of the materials that becomes unusable. Furthermore, recycling costs energy and other inputs. The input of new feedstocks will therefore always be necessary.

Figure 5.10: A cushion, floating down the river towards the sea, something hopefully avoided in the near future. (Photo: Harriëtte Bos)

A final important aspect that needs to be mentioned is the problem of accumulation of (plastic) waste on land an in the oceans (Figures 5.9 and 5.10). If we are going to design new materials of new renewable feedstocks, we need to take the utmost care that these will be intrinsically biodegradable and will not add to the ever-increasing blanket of fossil-based waste that covers our entire planet. Together with an increased awareness that the generation of waste needs to be reduced drastically, this can hopefully turn the tide of ocean pollution.

6 The materials transition, a joint task

In the previous four chapters, our story was very much focussed on the technological options that exist or are under development for the eventual replacement of the materials we produce nowadays from fossil feedstocks. We have shown that there are promising solutions for alternative production routes towards our materials, but many of these solutions are still in an early stage of development. It will definitely take many years before they have developed into mature technologies, and many may not reach a mature stage at all, because they run into hurdles that cannot be tackled. Maturing of technology is not just a matter of technological development; scaling up and successful market introduction requires interaction with other stakeholders such as financers, other companies, government and eventually also the consumer. This implies that in the transition towards fossil free materials each of us has a role to play. However, because the production chain of many of the materials described in the previous chapters are typically quite long, it is difficult for each stakeholder to realize their potential power to change things.

As an illustration of this, in Figure 6.1 a schematic view is presented of stakeholders of a typical fossil free production, use and recycling value chain from the perspective of packaging materials. The image clearly shows the complexity due to the large number of, and large variety in, stakeholders.

Carbon-based packaging materials generally consist of either plastics or paper and board. Two different production chains are involved in making these materials. Both are visualized in the brown arrow in the image: the plastics chain is depicted on the left front side and the paper chain on the left hind side. The plastics chain includes the production of biomass feedstocks, which then feeds into the biorefinery, where separation of the different components of the feedstock takes place, for instance into a carbohydrate fraction (sugar or starch), a protein fraction (that can be used for food or feed) and lignocellulose, that can either be regarded as a side stream or might be separated further into lignin, cellulose and hemicellulose. The carbohydrate fraction may go into the (bio)chemical industry, where building blocks are produced, from which a polymerisation plant makes a polymer (see Section 3.5 the building blocks pathway). The polymer is then processed into a plastic suitable for producing packaging material and goes to the packaging producer. Next to this possible route, also the recycling and CO_2 pathways may provide new feedstocks for this production route (see also Sections 4.3 to 4.5 and Sections 5.3 and 5.4)

For the production of paper-based packaging material, the paper and board industry starts from the production of wood or other natural fibres, the production of paper pulp from these feedstocks and subsequently the production of paper or board that then goes

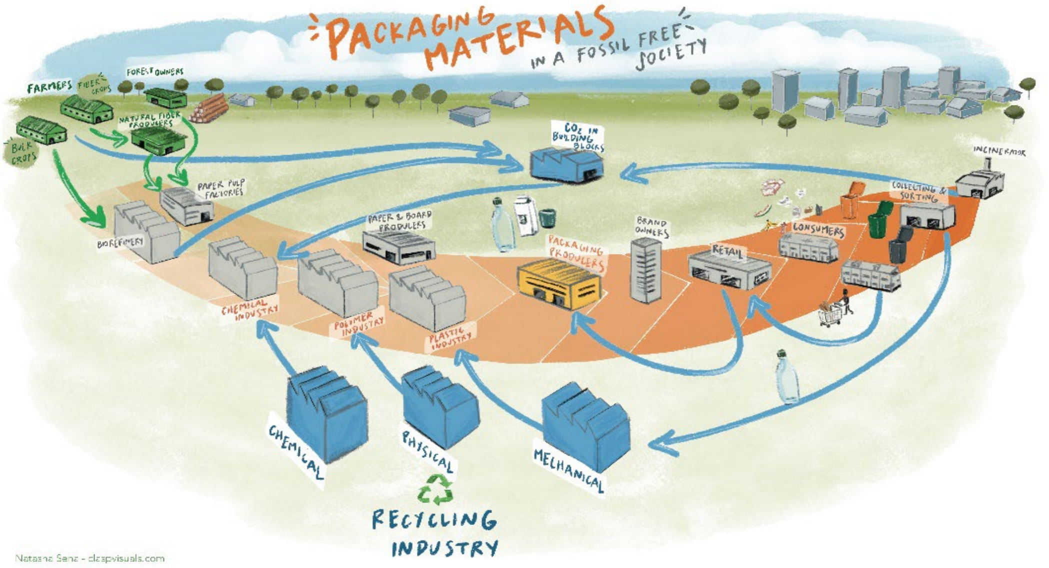

Figure 6.1: A visualisation of the fossil free packaging production circle, including the three pathways, biomass, recycling and CO_2, and depicting the role of consumers.

to the packaging producer. However, not only wood or other natural fibres are used as feedstock (Section 3.3), also the (mechanical) recycling of paper and board is part of this production chain, including of course the collection of waste paper by consumers (Section 5.2). When a packaging consists of a combination of paper and plastic these two chains converge at the packaging producer. Brand owners that package their products and retail them are depicted on the right side, followed by the consumer, who has influence over the entire system by buying or not buying a specific product. Furthermore, the consumer has a role in the recycling pathway, by means of his/her effort to collect and separate products after their end-of-life. And, of course, the consumer is also a voter and thus has an influence on politics and indirectly on legislation.

This whole production system is thus interwoven at various points, which are interdependent. And to make matters even more complicated, a change in feedstock early in the production chain inevitably means that other stakeholders in the chain also have to adapt their processes.

Today, the feedstock for most of the plastics is fossil oil and comes from the oil refineries. Changing our present system to the fossil free production system as visualised in Figure 6.1, will need changes in feedstock demand, technologies and processes in the industry, guided by the proper regulations from governments and supported by the (sustainable) purchasing behaviour of retail and consumers.

To further complicate matters, other markets or products, such as textiles, are partially based on the same feedstocks and stakeholders, for instance in the chemical sector, but also involve a large set of other stakeholders (see Figure 6.2).

The producers of the materials for synthetic fibres (left on the front of the brown arrow) are more or less the same stakeholders as for the (synthetic) plastics for packaging materials. The fibre spinners, however, are different companies, as are of course the yarn producers and the fabric producers.

The stakeholders producing natural fibres for textiles (left side, at the back side of the brown arrow) are very different from the pulp and paper industry that produces for packaging materials. The feedstock is produced by the growers of natural fibres like flax (for linen) and cotton. Processing these fibres into yarns for fabrics, is done by

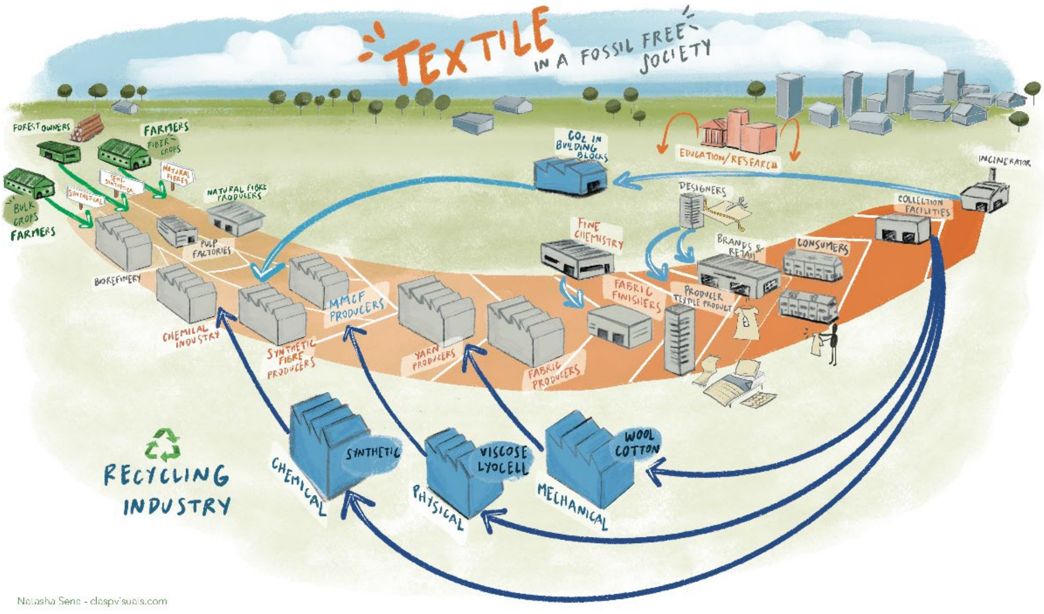

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Figure 6.2: A visualisation of the fossil free textile production circle, including the three pathways, biomass, recycling and CO_2.-

companies that clean the natural fibres and turn them into a sliver[55]. The sliver goes to the yarn producers, may be mixed with synthetic fibres and is subsequently turned into a yarn from which a fabric can be produced. Next to that, a small but significant fraction of textile fibres are the regenerative fibres, such as viscose and Lyocell, also known as MMCFs or Man Made Cellulosic Fibres (see also Section 3.4). The stakeholders involved in producing these are again very different: forest owners that produce wood, pulping factories that produce very clean cellulose and dedicated spinning factories that produce the MMCFs.

All these three groups of stakeholders supply the yarn producers that may mix different fibres and produce all kinds of yarns. Not discussed earlier, but also very relevant are the suppliers of a myriad of fine chemicals that are used during production of the yarns and fabrics, ranging from dyes to all kind of chemicals that improve the ease of processing and quality of the fibres. As with packaging, again the whole production system is interwoven at various points. Also here recycling and CCU technologies may provide part of the feedstocks.

An important group of stakeholders in textiles are the designers, as they may influence the type of fabric that is used for a specific garment or other textile application. And then of course there is us, the consumers who can influence the whole system by our buying (and disposing) behaviour.

Each application area, ranging from packaging and textiles to building materials, materials in automotive, in agriculture, sports, home and leisure and electronics, thus has a specific set of stakeholders involved in production and application. Some of the stakeholders, such as the chemical industry, may supply to different application areas. Many of the products produced are bought by consumers and therefore end up in our houses, where we dispose of them when they are worn, broken or just out-of-fashion, or have served their purpose. The service life of the products may vary significantly (compare packaging and furniture for example) but eventually they will be discarded and hopefully the materials they consist of will be reused in a new product.

Now the most pressing question is "how are we going to change the course of this production system into a sustainable direction". As stated early in this chapter this is not only a task of industry, design and retail, but of government, policy makers and consumers as well. If we want to make the transition towards a fossil free society into a success, a more or less coherent action from all these stakeholders is urgently needed.

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[55] More information on this process is given in the groene grondstoffen publication Textiles for Circular Fashion Part 1: Fibre resources and recycling options. Paulien Harmsen and Harriëtte Bos.

For all actors involved, a better understanding of the complexity and all interrelations in a fossil free production system may help to define and steer purposeful actions. Therefore, we hope that by providing more insight in the structure and (inter)dependencies of a materials production system that is not based on fossil feedstocks, this booklet may serve as a small cog helping to speed up this transition.

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