Materials challenges and opportunities to address growing micro/nanoplastics pollution: a review of thermochemical upcycling

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ABSTRACT

Micro/nanoplastics have sparked attention in recent years due to their widespread presence in the environment. Currently, several waste valorization approaches are under development in order to upcycle micro/nanoplastics. Thermal conversion technologies such as pyrolysis, gasification, liquefaction, or hydrothermal carbonization can yield high-value solid products, oil, and gases from plastics waste. The common thermal conversion technologies investigated focus on maximizing the production of oil and gases (such as H_2 and CH_4) for use as fuel. Except for hydrogen, when these products are used to generate energy, the carbon emissions generated are comparable to those produced by traditional fossil fuels. Herein, we present a review of the current efforts to capture and convert plastic waste into valuable products with an emphasis on identifying the need to develop processes specifically for micro/nanoplastics while also preventing the release of CO_2 emissions. We identify the development of efficient catalytic materials as a critical research need for achieving economically viable thermochemical conversion of micro/nanoplastics.

1. Introduction

Plastics have become an increasingly present aspect of our daily lives. They offer valuable properties such as dexterity and diversity, while being lightweight and relatively inexpensive to produce [1]. Plastics are used in the manufacturing of everyday items such as clothing and cosmetics, and further play crucial roles in constructing transportation vehicles such as automobiles and airplanes. In medicine, plastic products are critical as antiseptic and disposable containers and instruments that provide a high degree of hygiene [2]. However, despite the value of plastics for today's consumers, the environmental impacts associated with plastics after-use have started to plague human society and jeopardize the ecosystem's balance [3].

Plastic manufacturing has seen incredible growth in the past century, from 2 million metric tons in 1950 to 348 million metric tons in 2017 [4]. Between 26 and 36% of the world's plastics are single-use, intended for immediate disposal [5]. This is particularly concerning when considering that most plastic items end up in the environment after use. Due to the toughness and durability of plastics, they stay there for centuries. Plastic degrades in around 500−1000 years [6]. Despite their usefulness in the medical sector, increasing plastic use has also been linked to adverse health effects, through plastic particle deposition in the human body [7].

1.1. Plastic health/environmental consequences

The long-term environmental and health consequences of plastics are currently not entirely understood, and current findings point toward several causes for concern. Environmental problems include the destruction of habitat for wildlife [8], hazard of ingestion [9], and plastic-facilitated transport of organisms to new ecosystems [10,11]. Human exposure to plastic pollution is shown to

affect the respiratory, circulatory, and lymphatic systems [12]. Accumulation can occur in the liver, kidney, and gut [12]. Plastic particle transport and deposition in the human body is proposed to cause endocrine disruption [13]. Carcinogenicity and endocrine disruption can occur when certain polymers and their associated additives are inhaled or ingested for an extended time [7]. Inhalation, ingestion, and cutaneous absorption of plastics and micro/nanoplastics have been identified as the three basic exposure modes. Fig. 1 shows a schematic approach to health issues caused by plastic and microplastic exposure. Respiratory-related disorders have been epidemiologically associated with inhaled polymeric particles, including nasal cavity cancer, airway impaction, respiratory disease, and lung cancer [14,15]. Micro/nanoplastics ingested through food products may have neurological and psychological consequences, including diminished parental behavior, self-reported sexual dysfunction, and neurotoxic reaction [16]. Plastics have been shown to have reproductive consequences including breast cancer, prostate cancer, decreased sperm count, ovarian cancer, and overall impaired fetal development [17,18]. Moreover, consumption may result in metabolic disease, bladder cancer, large bowel cancer, diabetes, liver disease, and more [15,19]. Macro and micro/nanoplastics used on the skin are primarily associated with irritation. The consequences on these systems may be profound with chronic exposure; nevertheless, a lot remains unknown about the implications on the human population [7].

1.2. Plastic pollution elimination strategies

Plastics are mainly produced from fossil fuels, and the transition to a carbon-neutral economy will require substantial shifts in the plastics life cycle. The European Commission unveiled the European Green Deal (EGD) [20] in December 2019, aiming to make Europe the first climate-neutral continent by 2050. In addition, the EU created the EU Taxonomy Regulation [21], which establishes criteria for what economic activities qualify as 'sustainable'. The regulations can contribute significantly to climate change mitigation while also contributing to other environmental objectives such as transitioning to a circular economy, waste prevention, and recycling. The EU Taxonomy Regulation EU) 2020/852 has developed a comprehensive list of waste-related activities that meet this criterion, notably excluding waste-to-energy incineration, and including waste prevention and recycling [22]. The United Kingdom follows the same strategy regarding zero-waste targets [23].
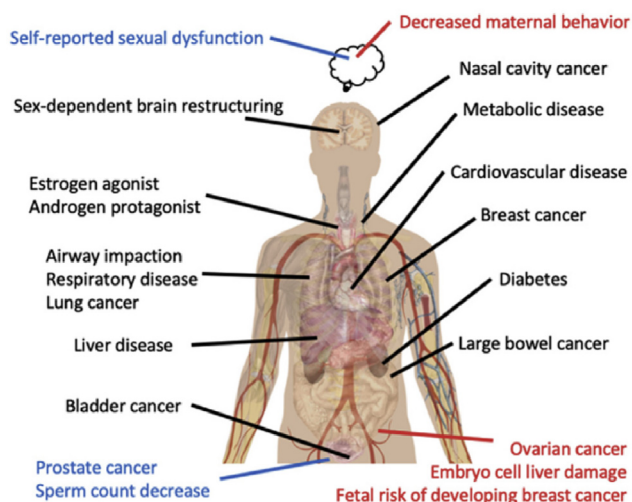

Fig. 1. Plastic and microplastic human health impacts [7].

Recently, it has been estimated that 8 million tons (Mt) of plastic waste reach the ocean each year [24]. This amount of plastic annually entering the ocean is expected to triple by 2040. Therefore, achieving an environmentally friendly and efficient strategy to eliminate plastic pollution is necessary [4]. The Break The Plastic Wave Report [4] estimates that it is possible to reduce plastic release to the ocean by 80% with an appropriate system change. In a proposed scenario (Fig. 2), it is proposed to reduce the utilization of plastic by 30%, substitute plastics with other materials by 17%, and recycle 20% more through chemical conversion in order to become closer to a zero-waste system. While scaling up recycling is vital, it is not technically or economically feasible to completely eradicate plastic pollution by recycling all plastic items [4]. The value of mechanically recycled plastic is limited by the quality criteria for food-grade plastic. Most plastic can only be mechanically recycled two or three times before deteriorating in quality [25]. This is not a technological limiting factor in chemical conversion where plastic polymers are transformed/depolymerized to their fundamental molecular building blocks. It is estimated that 20% of plastic waste may be suitable for chemical recycling [4]. Plastic-to-plastic chemical conversion enables the reintroduction of waste into the petrochemical process to make plastic, lowering the demand for petrochemical raw materials extraction [26]. On the other hand, substitution of alternative and less environmentally harmful materials to plastic should be examined wherever feasible to lower the use of plastics. Substitutes are often more expensive than plastics, and their carbon footprints vary depending on the material/geography [27]. Designing materials for reuse, recycling, and biodegradation is another necessary action item. Even after adopting a proposed scenario as in Fig. 2, including the reduction, substitution, and recycling of plastics, it is estimated that approximately 30% of plastics will be disposed of and mismanaged. To reduce the amount of disposed of and mismanaged plastics, innovation and research are needed [4].

Numerous indigenous microorganisms, such as bacteria and fungus, present in wastewater sludge, soils, and landfills can biodegrade manufactured plastics. Microorganisms can utilize these monomers and oligomers as substrates to produce biomass and carbon dioxide under aerobic conditions [28], through the process of microbial biodegradation. However, the output gasses streams of aerobic and anaerobic metabolism lead to increased carbon dioxide emissions. Another drawback of simple biodegradation is the slow rate, which is not sufficient to handle the massive amount of plastic that has been generated and accumulated already and is continuing to be released to the environment [28]. The shift of the current scenario needs to be achieved with a collective effort to develop and innovate different waste management technologies simultaneously.

Waste collection innovations can assist in resolving a variety of issues, mainly helping prevent leakage to the environment. New garbage aggregation models, improved communication with waste producers, and improved logistics for collectors can make waste collection more efficient. In addition, decentralized waste storage, processing, and treatment can empower residents while redirecting resources away from trash disposal and minimizing the possibility of mismanagement [4]. Once the waste has been collected, it needs to be processed to prevent the release of both plastic and any derived greenhouse gases into the atmosphere. This is where plastic 'upcycling' can be a solution, which is the focus of this review.

1.3. Plastic recycling/upcycling

Material properties greatly influence approaches to upcycling. In the case of plastics waste, the material properties are
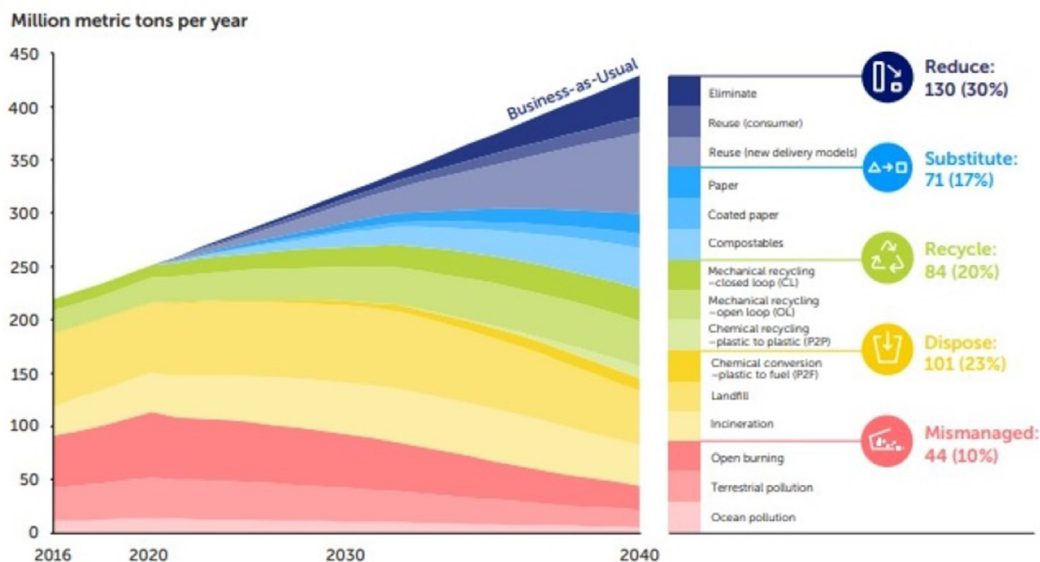
Fig. 2. Plastic in the system change scenario proposes for the break the plastic wave report. Including micro/nanoplastics and macroplastics [4].

determined by the polymers and additives that are combined to form plastics. Plastics are generally classified into two types: thermoplastics and thermosets (Fig. 3) [29]. When heated, thermoplastics melt and flow; when cooled, they solidify. This heating and cooling process can be repeated numerous times, and thermoplastic materials are generally melted first to reprocess them. High-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) materials are widely utilized in the manufacture of a variety of consumer goods, including lids, carrying bags, and fast-food packaging. Polyethylene terephthalate (PET) is used to make bottles for carbonated beverages. Polyvinyl chloride (PVC) is utilized to manufacture flooring, footwear, and bottles. These are mainly single-use plastics [30]. Furthermore, unlike thermoplastics, thermoset materials cannot be remelted and will decompose rather than melt. This is because they are chemically bonded during the curing process. This results in a chemical structure that is highly dense, imparting stiffness, and brittleness. Additionally, they have a longer useful life (10 years or more) and are utilized in smaller amounts than thermoplastic materials [31]. Due to the different categories and types of plastics with completely different properties, separating them before any recycling process may be necessary. Furthermore, it has been shown that combined polymers are chemically incompatible with one another [31]. The required different temperatures to melt and process them are also key considerations for remelting them as a mix in the case of different types of thermoplastics. Otherwise, if thermoplastic is reprocessed and mixed with thermoset, the mixture will not be homogeneous, resulting in a portion of the materials (thermoset component) decomposing, creating losses in process efficiency and economics as the energy is expended toward decomposition rather than toward melting the mixture [31].

Most plastics disposed of and mismanaged eventually degrade under weathering and aging into micro/nanoplastics. Micro/nanoplastics are widely detected in marine and coastal environments and are defined as plastic debris with less than 5 mm in size. Micro/nanoplastics have gained increased attention in recent years as they are present everywhere in alarmingly large quantities [32]. Currently, micro/nanoplastics are categorized according to their origin into primary and secondary micro/nanoplastics (Fig. 3). Due to their small size and large surface-to-volume ratio, micro/nanoplastics can also sorb and accumulate pollutants which they can then transfer to organisms, causing toxicity across the food chain [32].

Mechanical recycling is the most prevalent form of recycling for plastics. Initially, recovered plastics are crushed down to a size suitable for reprocessing/mechanical recycling. This has been a long-standing practice in the plastics industry's manufacturing facilities. This recycling process, termed primary recycling, makes economic sense since manufacturers eliminate their own waste and increase production yields [33]. Secondary recycling entails a reprocessor reclaiming used material from various sources. Material may come in several shapes and sizes, including bales, moldings, and enormous plastic lumps. To an acceptable feed supply size, size reduction, cleaning, sorting, and regranulation may also be required [34]. Chemical recycling is breaking down polymers into smaller molecules that may be readily separated from contaminants. This technique, also known as feedstock recycling or tertiary recycling, produces raw materials for petrochemical operations or feedstock that may be utilized to make monomers for new polymers or other petroleum products [33]. Finally, thermochemical processing, also known as quaternary recycling, is the conversion of solid wastes into conversion products with the discharge of heat energy. It may be used for two things: volume reduction and energy recovery [1,34,35]. It should be noted that all of the above forms of recycling are complementary to each other and potentially necessary to achieve a circular economy [4].

Quaternary recycling has been one approach for plastics pollution mitigation that has gathered attention in the scientific community. It is also called 'upcycling', where plastic waste is converted into different products of greater value. Thermochemical conversion technologies such as pyrolysis, gasification, liquefaction, or hydrothermal carbonization have been explored in this approach, to obtain valuable oil and gases from micro and macroplastics [1,35]. Although thermochemical conversion appears promising when dealing with mixed discarded plastic, it usually occurs at high temperatures (300−800 °C). Catalysts may play an essential role in increasing thermochemical conversion energy efficiency, encouraging focused reactions, and enhancing product selectivity [36]. Furthermore, co-processing methods that
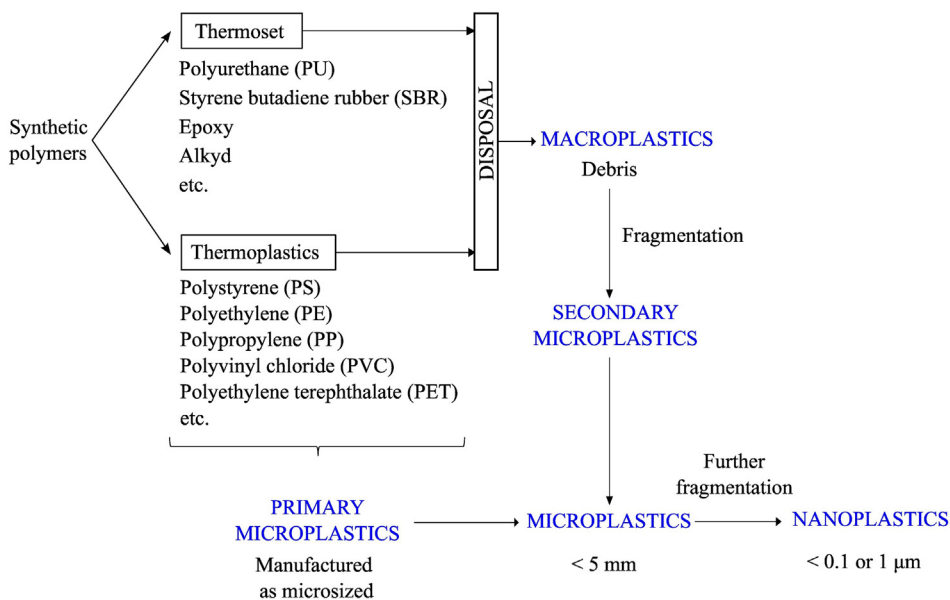
Fig. 3. Macro plastics and micro/nanoplastics composition [39].

include mixing of biomass with polymers, such as co-pyrolysis, co-liquefaction, and co-gasification, offer significant environmental and economic benefits [1]. In one application, researchers explored the properties of typical solid feedstock combinations, emphasizing elemental composition, proximate analysis, and heating value [37]. The various feedstocks' effective hydrogen to carbon ratios are analyzed to guarantee the quality of petrochemical equivalent products generated from co-pyrolysis of plastic wastes and biomass. HDPE, LDPE, and PP were found to have a positive synergetic impact on liquid yield in co-pyrolysis with solid biomass. In contrast, PET, PS, and PVC have a positive synergetic effect on solid waste or gas yield [38]. In another study, microplastic co-gasification with biomass was investigated to achieve a better-quality syngas production than when only biomass was used as a feedstock [37]. The previous research team carried out an Aspen simulation where higher H_2 content was obtained when microplastic fraction was higher than biomass, achieving a better quality syngas production [37]. Most thermal conversion technologies target the production of hydrocarbon oils and gases and sometimes H_2 [1,37,38]. When the resulting hydrocarbon fuels are combusted to generate energy, the carbon emissions are similar to traditional fossil fuels.

Nevertheless, by using efficient and selective catalysts in the thermochemical conversion of polymers, the operating temperature requirement may be significantly reduced while increasing carbon conversion and process efficiency. Hence, with the suitable catalyst, thermal conversion technologies can be optimized in order to maximize H_2 production and minimize oil fraction. In addition, it is possible to target valuable solid products that 'trap' the carbon rather than release it, such as through the production of carbon black or carbon nanotubes [40,41].

Herein, we provide examples of current initiatives to upcycle microplastic waste into energy carriers (such as H_2) and valuable solid carbon products. A thorough analysis of the different types of micro/nanoplastics, collection devices, viable products, and waste valorization techniques, including the advantages and disadvantages of the processes, are provided. While prior research has focused on the broader applications of pyrolysis, bulk-plastic upcycling, or non-thermal pathways for plastic conversion, the present review is focused on emerging thermal conversion

methods for micro/nanoplastics such as pyrolysis, gasification, hydrothermal carbonization, and liquefaction, presenting a more detailed analysis of these techniques. There are present in the literature reviews for the interested reader, focusing on bulk plastic upcycling or non-thermal pathways for plastic recycling [42–44].

2. Micro/nanoplastics

2.1. Micro/nanoplastics classification

Micro/nanoplastics are defined as untreated waste with a diameter of less than 5 mm in size that have a significant synthetic plastic content. They have gained increasing attention due to prevalence in the environment and their possible detrimental effects on animals, humans, and ecosystems [45]. Microplastic contamination in the environment is classified by source as primary and secondary. Fig. 4 shows the different release mechanisms for micro/nanoplastics and common changes in their physicochemical structure after being discarded.

Primary micro/nanoplastics are purposefully produced as microscopic particles and are directly released to the environment by sewage spills or home and industrial effluents [46]. Primary micro/nanoplastics can be composed of plastics pellets, nurdles, powders, and fibers used as personal care and cleaning products additives or industrial materials. These particles have rounded or amorphous shapes. For example, microbeads can come from facial scrubs; artificial microspheres are used in cosmetics and detergents and artificial resin pellets are used as raw materials for industrial purposes [47]. Fig. 4 shows the common processes and products that use them, resulting in primary micro/nanoplastics released into the environment.

Secondary micro/nanoplastics arise from the degradation of larger plastic pieces. The disintegration of these polymers is driven by UV radiation, thermal aging, bio-film growth, and oxidation [48]. Degradation is a term that refers to a sequence of chemical events that result in the breakdown of the structures of plastic polymers. It is further classified into photodegradation, thermal degradation, biological degradation, and thermo-oxidative degradation. These micro/nanoplastics are produced

mainly by breaking down plastic items extensively utilized in packaging, construction, agriculture, transportation, textiles, and household products [47].

Additional degradation of primary and secondary micro/nano-plastics alters their characteristics, affecting their physical and chemical properties. The changes in properties such as color, surface morphology, hydrophilicity, crystallinity, particle size, and density, directly affect environmental interactions. The degree of crystallinity of polymers directly affects their mechanical characteristics. Semi-crystalline polymers are durable and resistant to abrasion, while amorphous polymers are soft and flexible. Moreover, micro/nanoplastics having a low density will float in the water column, whereas those with a higher density than water would sink and deposit as sediments. Some studies demonstrated that micro/nanoplastics of small size (0.02−1 mm) and with lower density are more abundant than heavier and larger ones. However, the density and grade of crystallinity of micro/nanoplastics are properties that easily change with weathering and aging processes [32,49].

Microplastic polymers are typically composed of PE, PP, PS, PVC, and polyester (PET) and can sometimes contain acrylic [47]. The chemical structure and composition of some of these polymers are depicted in Fig. 5 [50]. The elemental composition of these polymers contains mainly carbon and hydrogen.

Furthermore, it is crucial to pay special attention to one of the main sources of microplastic generation, textile fibers, schematically illustrated in Fig. 6. There are three main types of fibers: natural, obtained from renewable resources such as cotton (cellulosic) and wool (protein bases) that do not contribute to micro/nanoplastic pollution; synthetic, derived mostly from non-renewable petrochemical resources such as polyester and nylon that contribute to micro/nano plastic pollution; and semi-synthetic or regenerated, produced from dissolving cellulose from wood and other sources to spin filament cellulose fibers. These fibers have different names depending on the process and solvent used (rayon, lyocell, Tencel) [51]. In fact, 63% of textile fibers are sourced from petrochemicals and synthetic fibers, such

as nylon, acrylic, polyester, and PP. The manufacturing and disposal of synthetic fibers generate significant amounts of carbon dioxide emissions [52]. Cotton dominates the remaining 37% of fibers produced. Microfibers from synthetic fabrics are released throughout clothes manufacturing, usage, and disposal stages of clothes [53]. Microplastics derived from laundering make up 35% of the total micro/nanoplastics emitted to the ocean from primary sources (Fig. 4). However, there are other textile micro/nanoplastics emissions to the air and soil that end up eventually in the ocean and are worth being considered (Fig. 6) [54]. In addition, it is necessary to add that micro/nanoplastics fibers are emitted to the air in the form of dust from clothing and emission of particles from clothing dryers. These microfibers will travel through the air into the ocean and the human respiratory systems [55,56]. From secondary sources, plastic items that exceed the 5-mm scale and enter the environment are known to deteriorate further, possibly producing micro/nanoplastics. This is true for fishing and aquaculture equipment and sanitary items [56]. Additionally, landfilling of synthetic clothes is another significant source of microfibers [53]. Fast fashion's disposable nature and throwaway culture have created a severe environmental, social, and economic crisis. According to the American Apparel and Footwear Association, more than 16 million tons of textile waste were created in the United States in 2015, with just 15% recycled, 19% burned for energy recovery, and the remainder (66%) thrown into landfills [56]. Synthetic polymer-based clothing is estimate to take 200 years to degrade in a landfill and first they will fragmentize into microplastics [56].

There are numerous reasons for recycling, reusing, and upcycling textiles and everyday clothing: (1) these wastes are valuable and reusable; (2) they contain materials that if recovered can conserve water and energy used to manufacture new clothes and textiles; (3) their recycling and reuse can reduce the carbon footprint and greenhouse gas emissions associated with the manufacture of new clothes; and (4) the waste would otherwise occupy a significant amount of space in landfills for a substantial amount of time [56].
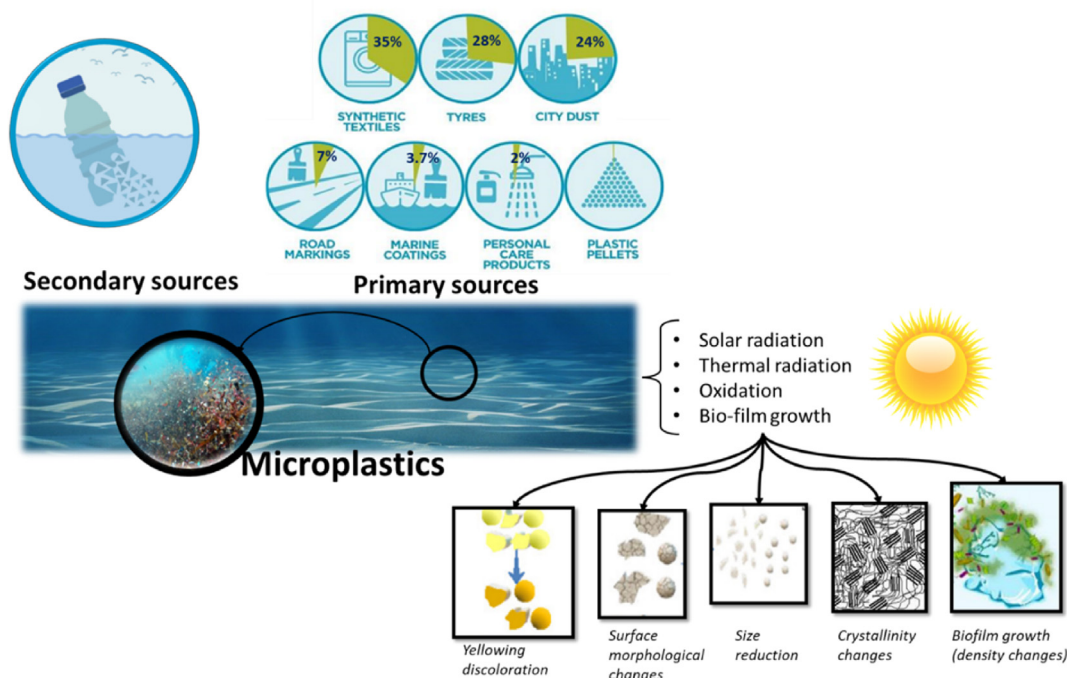

Fig. 4. Properties changes of micro/nanoplastics after degradation [modified from Refs. [32,49]].
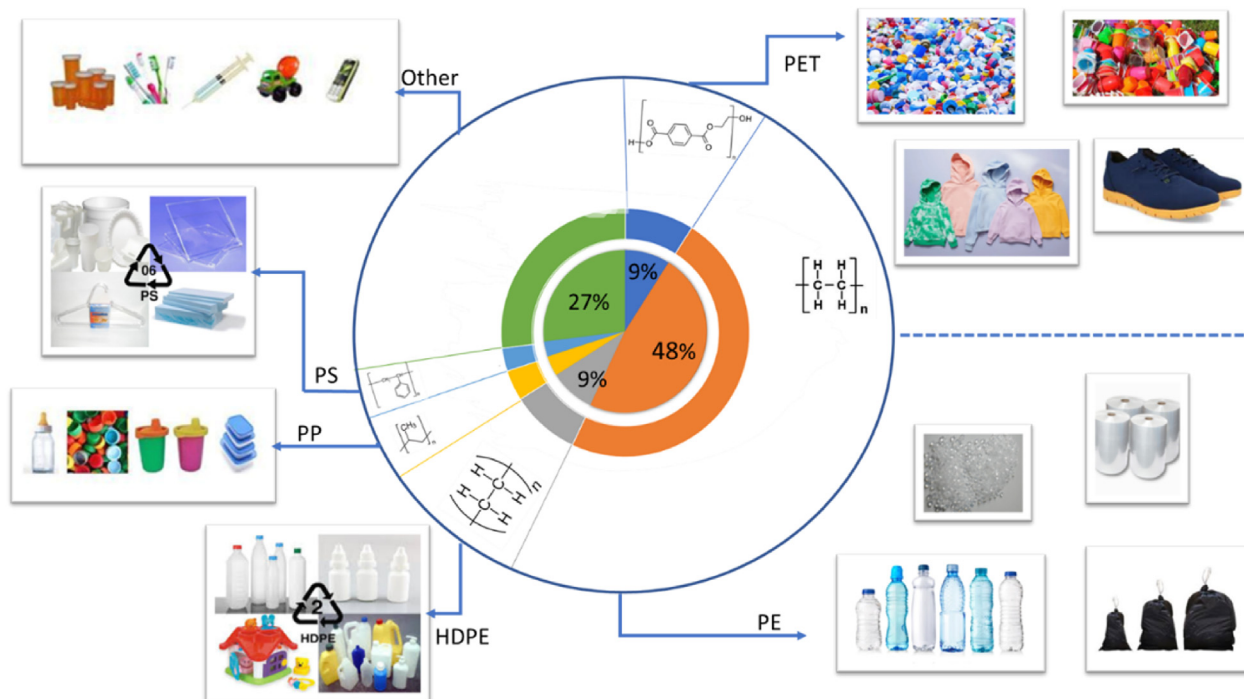
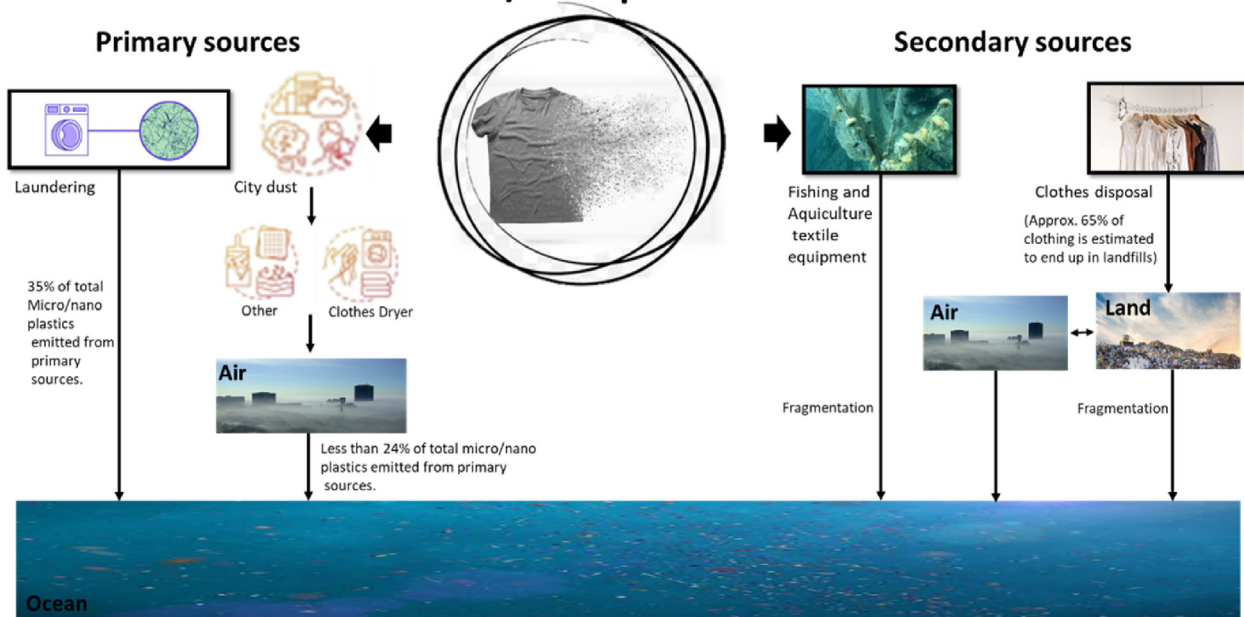**Fig. 5.** Common micro/nanoplastics chemical formulation [50].

Fig. 6. Textile microfibers sources [information from Refs. [53,54,56]].

2.2. Micro/nanoplastics collection devices

For micro/nanoplastics upcycling, first, it is necessary to collect them. In the case of the primary micro/nanoplastics, it is essential to capture them directly from the sources avoiding their emission to the aquatic environment. To abate secondary micro/nanoplastics pollution, it is crucial to develop technologies that can capture these efficiently. Several collection devices have been developed to

remove micro/nanoplastics from the aquatic environment [57]. There is currently no available solution to recapture particles released to the air and soil directly.

It is predicted that nearly 80% of microplastic in the open sea comes from sewage effluent discharges, wastewater treatment plant (WWTP) effluents discharges, and urban runoff [58]. Studies on micro/nanoplastics in municipal WWTPs show that the overall efficiency of existing treatment methods to remove microplastic

from water is estimated to be above 90% [58]. However, with these methods, most microplastic particles end up in a sludge that is generally applied on agricultural land as fertilizer and can enter waterbodies via runoff. Despite the high effectiveness of the treatment systems in removing micro/nanoplastic particles, the amount of microplastic particles discharged is a serious problem due to the large volume of wastewater treated [58].

Washing machine effluents constitute a significant source of micro/nanoplastics released into the aquatic environments. Synthetic fibers from textiles and microbeads from detergents can be removed or captured at the household level via devices that can be used while operating washing machines. There are several available commercial collection devices (Cora Ball and the Lint LUV-R filter are two examples depicted in Fig. 7) for decreasing fiber release from clothes washing. The methods shown in Fig. 7 have been reported to have 26% (Fig. 7a) and 87% (Fig. 7b) capture efficiency respectively, suggesting that their widespread implementation can create an ample yet distributed supply of collected micro/nanoplastics waste [58]. Micro/nanoplastics removal is not a currently regulated aspect of water treatment [59]. However, France recently introduced new legislation aimed to curb this pollution, requiring that by 2025, all new washing machines have a filter to capture plastic microfibers that fall off garments while washing [60]. In addition, in California, entities that operate industrial, institutional, or commercial laundry facilities are required to adopt the use of the best available control technology to capture microfibers that are shed during washing, as identified by the state board (Bills AB-802/AB-129). Australia committed in the 2021 National Plastic Plan (NPP) to work with the textile and white goods sectors on an industry-led phase-in of microfiber filters on new residential and commercial washing machines by 1 July 2030. Researchers have demonstrated that the installation of filters in washing machines in 97 homes of a small town of Canada connected to the WWTP found a significant reduction in microfibers in the treated final effluent after filter installation [61].

Regarding secondary micro/nanoplastics and primary micro/nanoplastics released to the aquatic environment, their collection and detection are highly complex. Flotation methods are currently used to extract micro/nanoplastics from sediments. Some examples are decanting, elutriation, aeration, centrifugation, froth flotation, air-induced overflow, separation funnel, and overflow [62]. Other collection methods reported are categorized depending on the removal characteristics, such as filtration and surface attachment methods (e.g. coagulation, flocculation, and sedimentation, electrocoagulation, adsorption, magnetization, and microorganism aggregation) [38]. Note that these techniques are mainly utilized presently to sample small quantities of micro/nanoplastics [38,62].

If widespread micro/nanoplastics collection is implemented in homes via washing machine collection devices, it will be necessary to prevent the release of these plastics back into the environment. There is no way of ensuring this, as the collected fibers or used filters can make their way to landfills. It is possible to use upcycling techniques to create valuable products out of the captured micro/nanoplastics if the filters and/or micro/nanoplastics can be collected from individual households. It may also be possible to use small-scale upcycling processes. Bulk plastics upcycling techniques can also utilize the carbon in micro/nanoplastics, so that it is not oxidized to CO_2 and released as a greenhouse gas.

3. Plastics valorization techniques

The main pathways investigated for plastics valorization are biochemical degradation of plastics and thermochemical processing [1]. The biochemical approach breaks the polymers into monomers and oligomers by enzymes but is typically only effective for cellulose and other natural polymer products. The thermochemical approach is based on converting the polymers into a mix of products consisting of gas, oil, and char/tar. This review paper seeks to identify opportunities in thermochemical plastics upcycling [1,28,63,64].

3.1. Thermochemical conversion of micro/nanoplastics

Most thermochemical waste conversion technologies under research use liquefaction, gasification, and/or pyrolysis. Some novel technologies are also being explored for plastic upcycling, such as hydrothermal carbonization, microwave-assisted conversion, plasma-assisted conversion, and photoreforming [63].

3.1.1. Liquefaction

Liquefaction is a thermochemical solid-to-liquid conversion method that converts waste organics to energy-dense oil at high pressures, often with catalysts and high-pressure H_2 [65]. The addition of H_2 increases the process conversion toward oil products [66]. Traditionally, liquefaction has been used to process biomass, achieving thermal decomposition at temperatures ranging from 250 to 450 °C and pressures between 1 and 20 MPa [67]. Biomass liquefaction is assumed to commence with the heat rupture of linking bonds with the subsequent production of free radical species. Hydrogen addition can pevent the recombination of radicals [68]. This approach can be applied to plastic waste. Liquefaction may also be conducted under hydrothermal high-pressure conditions. Hence, several liquefaction approaches have been developed for various solid waste valorization applications, and some of these methods have been applied to decompose plastics waste [63]. Therefore, the biggest drawback of using the liquefaction process to obtain oils is the use of high-pressure H_2 supply as a co-reactant to boost the conversion of the feedstock and make the process efficient [65]. In addition, the use of a high-pressure H_2 source imposes some safety and cost-related limitations. Another concern for this technology is the use of oil products as fuels, which will contribute to increased anthropogenic CO_2 emissions as the plastics are derived from traditional fossil fuels [69].

Liquefaction can be performed over a wide range of temperatures and pressures depending on the feedstock used [70]. An alternative way to perform the process is by eliminating the high-pressure H_2 source and adding a solvent that can work as a hydrogen donor for the system. Water is used as the aqueous reaction media and hydrogen source in hydrothermal liquefaction, known as hydrothermal carbonization, which is carried out at temperatures ranging from 280 to 370 °C and pressures ranging from 10 to 25 MPa [71].

Typically, waste plastic is co-liquefied in the presence of a biomass source to produce oil rich in aliphatic hydrocarbons [72]. Compared to alternative waste to value technologies, liquefaction of biomass results in a more even distribution of components among the products. Greater carbon content in the feedstock should improve fuel performance [73]. For any liquefaction process, the catalyst selection is critical and significantly impacts the process efficiency. In most situations, heterogeneous catalysts are used in the liquefaction process [74]. In liquefaction, alkali catalysts such as sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide may increase oil yields while reducing char production [75].

The catalytic liquefaction of plastics using hydrogen as co-reactant has been documented in some studies since 1996. One of the earlier research projects consisted of applying this method to a feedstock mixed with coal. The catalyst used included the protonated zeolite Socony mobil-5, ferrihydrite treated with acid, coprecipitated alumina-silica, and ternary ferrihydrite-Al_2O_3-
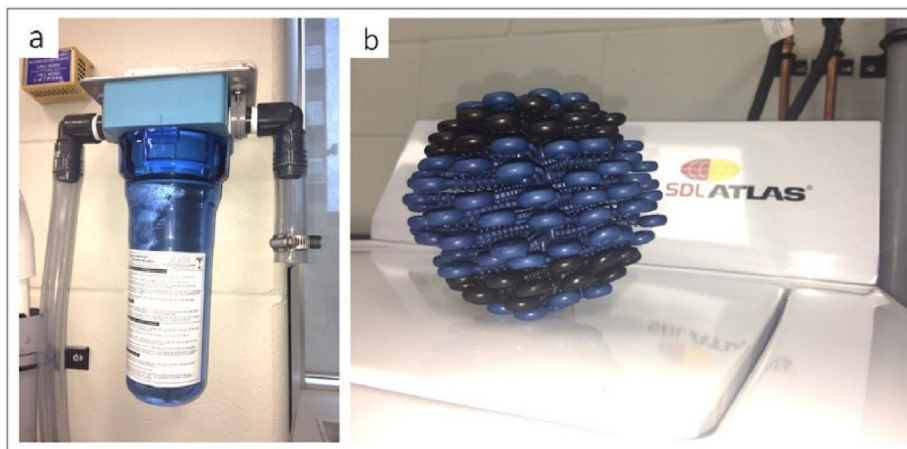
Fig. 7. (a) Lint LUV-R. (b) Cora ball [58].

SiO$_2$. The organic fraction obtained from the process was gasoline, kerosene, and heavy oil and the selectivity toward lighter hydrocarbons in the oil increased with the H$_2$ pressure [76,77]. Other related studies have been reported (Table 1), and a thorough and detailed literature review of this technique can be found elsewhere [1].

When plastics are liquefied, more viscous oil is generated than when lignocellulosic biomass and other biogenic wastes are pyrolyzed to create highly oxygenated oil. Additionally, the low oxygen content of oils generated through plastic liquefaction contributes to their heating value and fuel qualities. Because plastic-derived oils have a low moisture content, catalytic fuel upgrading procedures such as hydro processing, hydrotreating, and hydrodeoxygenation are often far less energy-intensive [74].

Pei and colleagues co-liquefied microalgae Spirulina in subcritical and supercritical ethanol with a synthetic polymer, HDPE. A mixture of microalgae and HDPE was liquefied together to make an oil rich in aliphatic hydrocarbons. Elevated pressure may also inhibit intermediate condensation, cyclization, and repolymerization [72]. High pressures used during liquefaction may prevent the production of the gas phase hence boosting the output of liquid oil [78].

Commercial application of this technology was established in 2000 by Sapporo Plastic Recycling ("SPR") in Japan. SPR constructed a plastic liquefaction plant with the potential to recycle over 50 tons per day of mixed plastic waste. The advanced thermal method recovers light oil used as a chemical feedstock for the manufacturing of new polymers, a medium fuel oil similar to diesel, and heavy oil used to produce power for export to the grid from this waste stream [79]. In addition, Klean Industries designs and builds facilities that transform waste plastics into premium oils in Canada. Their technology employs a continuous liquefaction process that indirectly heats plastic waste and a catalytic reaction to produce hydrocarbons, which are subsequently condensed to produce standard diesel and a patented heating fuel mix. These oils are compatible with diesel engines and generators without modification. Each ton of waste plastic may be converted into about 950 gallons of premium diesel fuel at a Klean facility. Diverse polymers may be treated concurrently without sorting, and common impurities such as grit, paper, metal, food residue, and oils do not need to be removed prior to processing. The improved method can accommodate large loads of PVC, PET, and optimal polyolefin polymers without causing reactor damage [79].

3.1.2. Hydrothermal carbonization

Hydrothermal carbonization (HTC) is a relatively recent approach to treating wet organic waste. HTC (also referred to as wet pyrolysis) is attracting attention also for the valorization of polymeric waste. The technology has a maturity of almost 110 years and is a way of mimicking the natural phenomena of mineralization in aqueous media, as in coal formation from natural biomass [85].

HTC products are gases (or incondensable vapors), liquids rich in absorbed inorganics and unreacted components from the reactants and solids rich in carbon (akin to coal) [85]. Modern applications of HTC have used various waste forms of biomass, municipal solid waste, plastics, and bulk textiles as the reactant, aiming for solid carbon, different gases (such as CO$_2$, CO, CH$_4$ and C$_2$H$_4$), and oil products [86]. Applications of the process have been successful in producing solids rich in carbon with microporous structures, and nanomaterial forms. Further inspection of the integral structure of the solids indicates the existence of functional groups of oxides, sulphides, halides, based on the selection of feedstock used [85].

Subcritical and supercritical water are two fluid states of water that are used in hydrothermal liquefaction and gasification processes [87]. Wet feedstocks can react in subcritical water at 180−260 °C to form hydrochar, a highly carbonaceous substance, utilized for energy production and agriculture, as activated carbon adsorbent among other applications [88]. Subcritical water acts as a solvent and reagent in organic chemical reactions. Hydrolysis is the first stage in the hydrothermal treatment of organic matrices, continued by defunctionalization processes, including dehydration and decarboxylation, and eventually recondensation and aromatization [89]. Due to the high ionic strength of subcritical water, between 180 and 280 °C, it works as both a reactant and a catalyst, promoting feedstock dissolution and recondensation into solid products throughout the HTC process. The solid products might be utilized as coal alternatives [89]. Research effort have demonstrated that when HTC process use PVC as feedstock, aliphatic and alicyclic hydrocarbons, benzene, naphthalene, diphenyl, phenanthrene, pyrene, and their alkyl derivatives, in addition to valuable platform chemicals such as acetic acid, furfural, lactic acid, propionic acid, phenolic compounds, hydroxymethylfurfural, levulinic acid, formic acid, and succinic acid may be found in hydrochar [90]. Water is an excellent solvent for hydrothermal conversion processes, due to its low cost, non-toxicity, and abundance [91,92]. Organics are hydrolyzed into low molecular weight molecules during HTC. Due to the deconstructed molecules' instability and reactivity, they repolymerize into high molecular weight compounds [1].

Table 1
Plastic liquefaction experimental results.

Year/Author	Feed	Co-reactant	Pressure (MPa)	Temperature (°C)	Catalyst	Residence time (min)	Products	Ref
Feng et al. (1996)	Coal/PPE, PPE, PP, PP/coal, PP/PPE, PP/PPE/coal	Waste oil/tetralin mixture	5.6–0.7	420–460	HZSM-5 zeolite catalyst, ferrihydrite treated with critic acid, Al_2O_3-SiO_2, ternary ferrihydrite, Al_2O_3-SiO_2	20–60 min	Gasoline, kerosene, heavy oil	[77]
Luo and Curtis (1996)	LDPE, HDPE, PET, PS. Mixture with coal	Tetralin/hexadecane or none	2.8–8.6	400–440	HZSM-5 zeolite catalyst, Al_2O_3, super nova-D, Octacat, Octacat-50G (fluid catalytic cracking catalyst)	30–120 min	Benzene	[80]
Zmierczak et al. (1996)	Plastics and rubbers (PS)	NA	3.4–17.2	350–450	Solid superacid catalysts: ZrG_2/SO_4^{2-} and Fe_2O_3/SO_4^{2-}	15–120 min	Benzene, ethylbenzene, toluene, alkylbenzene, naphthalenes, and other hydrocarbons	[81]
Shabtai et al. (1997)	HDPE, PP, polybutadiene	NA	3.4–13.8	350–450	Solid superacid catalysts: SO_4^{2-}/Fe_2O_3, SO_4^{2-}/ZrO_2, SO_4^{2-}/Al_2O_3, and a Pt-modified SO_4^{2-}/ZrO_2	30–180	Benzene, alkylbenzenes, tetralins, indanes and bicyclic arenes, cycloparaffins and olefins	[82]
Pei el al (2012)	Spirulina/HDPE	Subcritical and supercritical ethanol	9.3–11.9	320–380	Non catalytic	NA	Bio-oil rich in aliphatic hydrocarbons	[72]
Wang et al. (2014)	Lignite, wheat straw, and plastic waste	Subcritical water	2.0–5.0	260–320	Non catalytic	30 min	Benzene, asphaltene, preasphaltene	[83]
Wu et al. (2017)	Microalgae Dunaliella tertiolecta/PP	Subcritical and supercritical water	NA	320–370	Non catalytic	0–40 min	Hydrocarbons, carbonyl compounds, acid, nitrogen compounds.	[84]

Other investigations have indicated a successful formation of hydrochar from non-catalytic HTC [93]. These authors conducted 3-h experiments at temperatures ranging from 200 to 300 °C using baby diapers as raw materials. The resulting gas accounted for less than 1% of the overall product mass, whereas the hydrochar and liquid phases accounted for about 10% and 90% of the total product mass, respectively. The process used water predominately as a solvent [93]. Further investigations have demonstrated that the quality of the solvent dictates the overall composition and grade of solid hydrochar produced [35]. However, the selection of the solvent is not limited to pure water. The use of seawater has been demonstrated as an effective method for producing value-added carbonaceous solids. In a study experimenting with using four types of plastics (polyethylene, PET, PP, and nylon), HTC was performed at low temperature (200−300 °C) and a constant residence time of 3 h using sea water as solvent [35]. Additionally, for HTC conducted at different temperatures (200 °C, 250 °C and 300 °C), the authors demonstrated that an increase in the process temperature led to a major increase in carbon content in the hydrochar, reducing at the same time its oxygen content [35]. Hydrothermal carbonization is typically performed in batch reactors with or without a catalyst. Fig. 8 shows the different HTC mechanisms that have been investigated for textile bulk waste processing. HTC of cotton and synthetic fiber in an autoclave reactor using deionized water as the solvent was investigated [86]. The specified reactor temperatures and residence times were 230 and 280 °C, for 30, 60, and 90 min [35,86].

Traditional HTC is susceptible to heat losses, non-selective heating, and uncontrollable side reactions, resulting in low yields and long residence times. However, it has been proposed the adoption and development of microwave assisted HTC (MHTC), can improve selectivity and reaction kinetics while achieving homogenous heat distribution [94]. The main drawback of MHTC is the low energy efficiency and high cost of the technology [94]. Additionally, co-HTC using lignocellulosic biomass has been suggested as a method to valorize PVC-containing medical waste. The organic chlorine in PVC may be converted to inorganic chlorine (hydrochloric acid, HCl) in the HTC process by hydrolysis, defunctionalization, recondensation, and aromatization. After washing the solid goods with condensed water, the inorganic-Cl with a high-water solubility may be eliminated. Lignin addition considerably increases the dichlorination efficiency in the HTC process [95]. SEM micrographs of PVC-derived solid fuels before and after HTC can be appreciated in Fig. 9 [95].

HTC is a promising thermochemical process for the production of solid carbon-rich fuel (hydrochar) and other high-value-added products due to the low temperatures required, and suitability for processing wet feedstocks, which can also be leveraged for micro/nanoplastics waste recovery in aquatic environments. While HTC can operate at lower reaction temperatures than combustion, pyrolysis, and gasification, it requires highly pressurized water, to enable the hydrolysis, aromatization, dehydration, recondensation, and decarboxylation processes resulting in the generation of high-value-added products [35]. In comparison with traditional liquefaction, this method does not require high-pressure H_2 and uses water as a hydrogen donor for the reaction. On the other hand, there is an environmental impact which needs to be considered, if the resulting hydrochar is combusted to produce energy.

3.1.3. Gasification

Gasification is a thermochemical process that transforms solid organic matter into synthesis gas. Synthesis gas, or syngas, is mainly composed of hydrogen and carbon monoxide, with some carbon dioxide [96]. Gasification could be carried out in the presence of air, steam, or aqueous media. While conventional
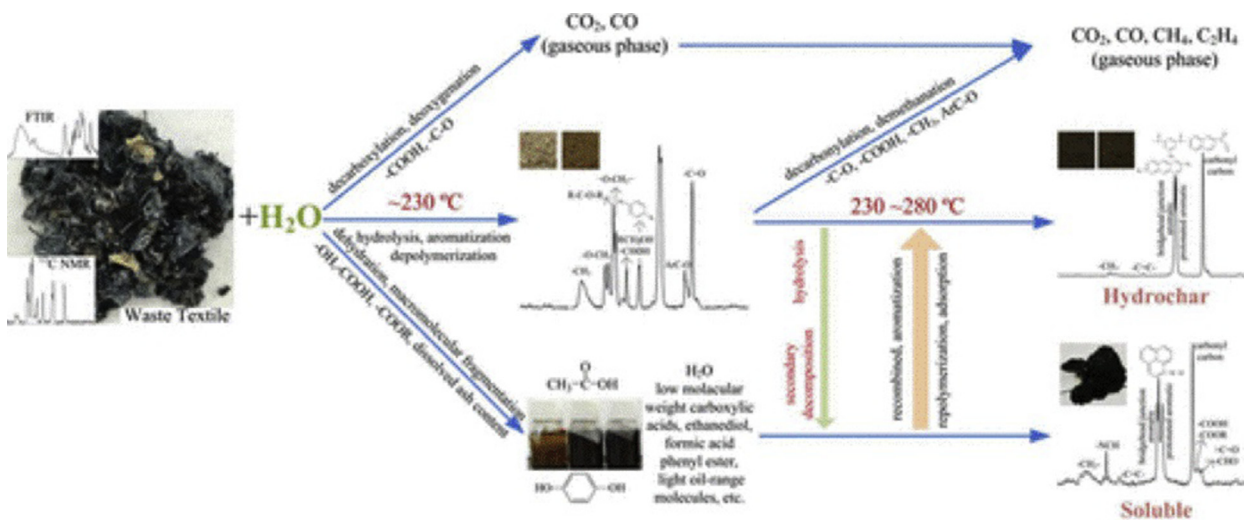
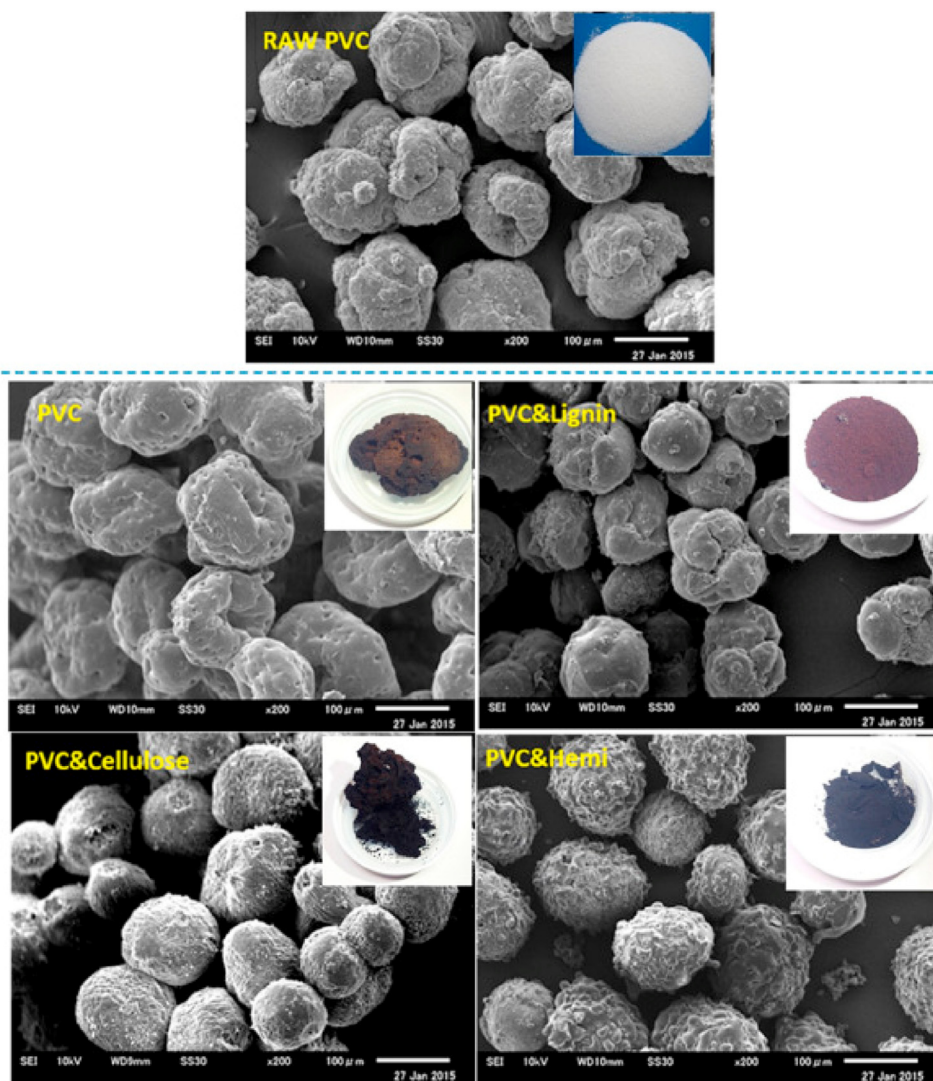**Fig. 8.** Mechanisms that govern the conversion of waste textiles using HTC [86].

Fig. 9. SEM micrographs of PVC-derived solid fuels before and after HTC [95].

gasification uses air or steam as the reaction medium, hydrothermal gasification uses subcritical or supercritical water [97]. Supercritical water's thermophysical features provide ideal conditions for the oxidation of organic wastes. Because supercritical water possesses the viscosity of gases and the density of liquids, it offers superior mass transport and solvation characteristics. Water behaves as a weakly polar solvent at its critical points, allowing for the hydrolysis of refractory organic molecules in a single homogenous phase [98].

Gasification in the conventional sense entails a succession of thermochemical processes, most notably partial oxidation, pyrolysis, and steam gasification. Conventional gasification extracts hydrogen from biomass and carbon [99]. With minimal pretreatment, conventional gasification can process heterogeneous and polluted plastics, and the syngas output may be utilized in various applications, including Fischer-Tropsch synthesis [100]. Gasification, like pyrolysis, may be used to convert plastic waste into high-value goods such as hydrogen and carbon nanomaterials, offering a path toward sustainable production of raw materials for nanotechnology applications and low emissions fuels [101,102]. Pyrolysis occurs when there is no oxygen present, resulting in the thermal cracking of organics to yield oil, gas and char. Partial oxidation on the other hand, utilizes oxygen lower than the stoichiometric amount necessary for complete combustion.

Furthermore, depending on the gasification agent employed, the process may be directed toward the creation of a gas fuel with a low heating value (when air is used) or a high heating value (when pure oxygen is used) or a hydrogen-rich syngas (using steam) [103]. Steam and CO_2 are utilized to produce H_2 and CO-enriched gases, because Steam may enhance the steam reforming of hydrocarbons, tar, and char in plastic waste gasification [36]. Steam gasification enables syngas production with a heating value of more than 15 MJ. Moreover, steam reforming may include partial oxidation and some water—gas shift processes [104]. Additionally, steam reforming converts hydrocarbons to syngas, similar to partial oxidation but with no oxygen present in the feed, only steam [105]. On the other hand, hydrothermal gasification, often involves several sub-reactions, including hydrolysis, steam reforming, hydrogenation, methanation, and the water—gas shift reaction. Hydrothermal gasification occurs by three distinct reaction mechanisms: (1) depolymerization of organic components, (2) breakdown of organic components via dehydration, link breakage, decarboxylation, and deamination, and (3) repolymerization of highly reactive components to tar [1].

Syngas yields are maximized at elevated temperatures and pressures, longer reaction durations, and low input concentrations. Because most gasification processes are endothermic, temperature significantly impacts gas product quality. Increased temperature boosts endothermic processes that create hydrogen, such as hydrocarbon reforming, tar cracking, water—gas reaction, methane (CH_4) breakdown, and steam reforming [106]. Hydrothermal gasification also produces a variety of liquid effluents, including acetic acid, propionic acid, butyric acid, phenols, aldehydes, ketones, methanol, ethanol, and furfurals [107].

Plastics' physicochemical features, such as low heat conductivity and high viscosity, may negatively influence gasification processes in general. Gasification reactors must be modified to enable better heat transfer and mixing to improve thermal degradation kinetics and avoid plastic agglomeration [103].

For plastics gasification, conventional gasifiers such as fluidized beds, fixed beds, and spouted beds have been adapted [108,109]. Two kinds of fluidized beds (bubbling and circulating) have been employed to gasify polymers. Furthermore, a two-stage fluidized bed system was used to catalytically gasify polymers into hydrogen and carbon nanotubes [101,110,111]. This technology may recover

plastic waste while also producing hydrogen and carbon nano-materials, if industrially viable selectivity can be achieved for such applications. Fixed bed reactors have also been utilized to gasify plastic waste due to their ease of operation and economic effectiveness [112]. For a series of investigations on syngas or H_2 generation from plastic pyrolysis—gasification, a two-stage fixed bed reactor was employed [113,114]. Moreover, the same reactor setup was employed to synthesize carbon nanotubes and hydrogen simultaneously. Using a two-stage reactor system, plastic waste may be converted to light hydrocarbons in the first reactor and then upgraded to hydrogen and carbon nanotubes in the second reactor [36].

Ebara environmental plant has created an industrial technique for thermally decomposing plastic waste and other high-calorific value waste into synthesis gas (carbon monoxide and hydrogen). The system consists of a pressurized gasification technology that combines a fluidized-bed low temperature gasification furnace with an industrial high-temperature gasification furnace. This technology allows the recovery of fly ash into molten slag that can be reused as a cement material. Similarly, Ebara has another technology that produces high-calorific value oil and gas mostly made of hydrocarbons from a range of carbon resources in the form of solid waste, ranging from high-calorific value waste such as bulk plastic to low-calorific value waste such as domestic biomass waste [115].

The main challenge faced during the gasification of waste is that the process is susceptible to the presence of impurities and contaminants in the feed stream because the resulting syngas quality can be significantly affected. Typically, H_2/CO ratios ranging from 0.8 to 1 are obtained in the syngas. Due to potentially high CO_2 concentration (25%), and high tar content (20−30 g/m^3), the syngas produced from waste gasification can require cleaning and conditioning before it can be utilized to make hydrogen, chemicals, or liquid fuels, adding cost to the overall waste valorization process [116,117] In addition, if air is used as a reagent, nitrogen present in the outlet stream will reduce the energy content and limit the applications of the gas products. Depending on the gasification conditions, other products such as oil and char can be produced. The deployment of catalysts in typical gasification processes seem to be unattractive, as their benefits (reduced coal and oxygen consumption, and lower heat losses) are outweighed by their additional costs [118].

The gasification of plastic waste is more expensive than mechanical recycling, there is incentive to target high value products to achieve economic viability [36]. The production carbon nanomaterials for example, offers a way to improve revenue while potentially sequestering carbon in the downstream manufacturing of products that can be used in diverse applications such as energy materials, electronic devices, and healthcare products.

3.1.4. Pyrolysis

Pyrolysis is a thermochemical solid-to-liquid conversion process that can be used to produce liquid hydrocarbon oils, char, and gas due to thermal decomposition of organic reactants under an inert atmosphere. The distribution of the products is highly dependent on the reaction temperature, heating rate, residence time, and reactor type. Unlike the HTC (batch) process, pyrolysis fluidized bed reactors are most often used because of their better heat and mass transfer capabilities, resulting in increased thermal cracking and high oil yields [1].

Pyrolysis produces oil that can be upgraded to be utilized as a fuel in vehicle engines, power plants or as a feedstock to produce fine value-added chemicals. Because pyrolysis oil is highly oxygenated, it has a low calorific value and energy density, and poor thermal stability [120]. Pyrolysis produces char as a solid

product, which is typically composed of stable aromatic carbon. Dehydration, deamination, decarboxylation, and dehydrogenation of organics during pyrolysis and gasification result in the creation of aromatic char [121]. Char's quality and applicability are governed by its physicochemical properties, including carbon content, degree of crystallinity, elemental composition, mineral matter, specific surface area, porosity, pH, electrical conductivity, and ion-exchange capacity. Char is burnt in a secondary combustion reactor to generate process heat in rapid pyrolysis demonstration and commercial processes [122].

Based on the heating rate and vapor residence time, pyrolysis reactions may be categorized as slow, rapid, flash, and intermediate pyrolysis reactions. Fast and flash pyrolysis are characterized by high temperatures (400−500 °C and 800−1000 °C, respectively), rapid heating rates (10−200 °C/s and 1000 °C/s, respectively), and short vapor residence times (30−1500 s and 0.5 s, respectively) producing more oil than char and gases. Slow pyrolysis is distinguished by its moderate temperatures (300−700 °C), slow heating rates (0.1−1 °C/s), and extended vapor residence times (10−100 min) leading to more abundant char production [119]. The commonly used parameters for pyrolysis have been summarized in Table 2. The average yield of liquid product or crude from pyrolysis was observed to increase with temperature. Plastic waste pyrolysis usually is conducted between 400 and 800 °C, at atmospheric pressure over catalysts [63].

The reactor type affects the mixing of polymers and catalysts, as well as heat and mass transfer. Additionally, the residence times employed in various reactors influence the product yields. For catalytic pyrolysis of plastic waste, fixed and fluidized bed reactors are preferable. Fixed bed reactors are frequently employed for catalytic pyrolysis of plastic waste on a laboratory scale [123−127]. Additionally, fixed bed reactors are used as secondary catalytic pyrolysis reactors due to the ease with which the products of primary pyrolysis can be fed into the fixed bed to undergo a two-stage process pyrolysis process [36]. On the other hand, multiple studies have shown the efficacy of fluidized bed reactors in overcoming the issues associated with fixed bed reactors [125]. Unlike fixed bed reactors, fluidized bed reactors include catalysts situated on a distributer plate that the fluidizing gas flows through, allowing the bed particles and catalysts to be fluidized. In fluidized bed pyrolysis of plastic waste, well-mixed catalysts with the fluid may give a higher surface area for reactions [128]. As a result, fluidized bed reactors are regarded as the most well suited reactor for large-scale operation, especially for catalytic pyrolysis and catalyst reuse [129].

Pyrolysis reactors for the thermal breakdown of tires are shown in Fig. 10. Reactors with a fixed, fluid, spouted, circulating, or transport bed are moved and rotated pneumatically. Ablative, centrifuge, auger, or screw reactors are put in motion mechanically and gravitationally [130].

Pyrolysis may take place in a one-stage or two-stage fixed bed reactor. In the case of a two-stage reactor, the first pyrolysis occurs in an inert gas environment (N_2), and the gaseous products are then driven down into the second half of the reactor, where catalytic reforming occurs in the presence of water vapor [130]. Wiltod and co-workers have demonstrated that the catalyst in the pyrolytic process enhanced gas production but decreased the yield of oil following a two-stage pyrolysis process of scrap tires. In the liquid

fraction, the zeolite catalyst enhanced the yield of single-ring aromatic compounds [130]. In another study, combining a fluidized bed with chemical vapor deposition has resulted in improvements for the manufacturing of high-quality CNTs [129].

Pyrolysis usually requires high temperatures, between 300 and 1000 °C [119]. The reaction can be performed at a lower temperature when a catalyst is employed. High temperatures cause dehydration, depolymerization, and fragmentation of polymers and other organics during pyrolysis, resulting in volatile components. When the volatile components condense, they are quenched to generate crude. The quenching procedure and the residence period of the volatile vapors influence the quality of the oil. Many degraded volatile chemicals are sequestered by rapid quenching and may condense, cleave, or react with other intermediate components at extended vapor residence time. Non-condensable gases such as H_2, CO_2, CO, and CH_4 escape in the product gas. The secondary reactions produce high molecular weight chemicals such as tars and char. Char and tar are hence the by-products of subsequent polymerization processes [131].

Over the last 40 years, review articles have been published covering the experimental characterization and kinetic modeling of plastic pyrolysis, such as those focusing on thermochemical conversion of plastic waste to fuel [1] plastic waste upcycling [63] and a recent study that describes an approach for kinetic modeling of thermochemical processing of polymers [132]. Pyrolysis is the thermochemical method that has been more broadly studied and used by the researchers in the past years due to its relative scalability compared to other options for waste valorization. Pyrolysis can be performed under atmospheric pressure in an inert atmosphere, avoiding the cost of pressurization and solvent use. At the same time, if the right catalyst is utilized, the reaction temperatures will be low, and the energy input for the process can be obtained from combusting a portion of the products, either gas, char, or oil [133].

One emerging approach for waste valorization is pyrolysis aimed at producing carbon nanomaterials. Currently, several review papers record the majority of the studies regarding plastic waste upcycling into high-value carbonaceous materials [134] and carbon nanomaterials [40]. One example study by Dan Xu and co-workers demonstrated the simultaneous production of aromatic rich bio-oil and carbon nanomaterials from catalytic co-pyrolysis of biomass and plastic wastes. The results determined that blending biomass with plastic feed increases the production of mono-aromatics and promotes the growth of carbon nanotubes (CNTs). The reactions were performed over a nickel catalyst supported on alumina [135]. A similar investigation was undertaken to convert non-condensable gasses from PP into carbon nanotubes and high-quality oil over a catalyst consisting of biochar. The temperature of CNT growth ranged between 500 and 900 °C depending on the catalyst particle size, with high temperatures and small particle sizes leading to better quality CNTs [136]. In contrast, Chenxi Wang demonstrated the production of hydrogen and liquid fuels from plastic waste over nanocellulose-derived biochar [137].

Yao and co-workers investigated the formation of high-value carbon nanotubes with clean hydrogen from waste plastic pyrolysis over a Ni-Fe bimetallic catalyst. Plastics were catalytically pyrolyzed using a two-stage fixed bed reaction system with Ni and Fe loading at different molar ratios. With a Ni:Fe ratio of 1:3, H_2 concentration and yield reached a high of 73.93% vol. The catalyst composition substantially impacted the volume and quality of CNTs, and Ni and Fe were found to play diverse roles in the overall activity for waste plastics pyrolysis-catalysis [41]. The process creating bamboo-like multiwalled carbon nanotubes from PP pyrolysis and catalytic breakdown and hydrogen production from PP aver a NiFe base catalyst have been investigated by Yao and Wang

Table 2
Pyrolysis parameters [119].

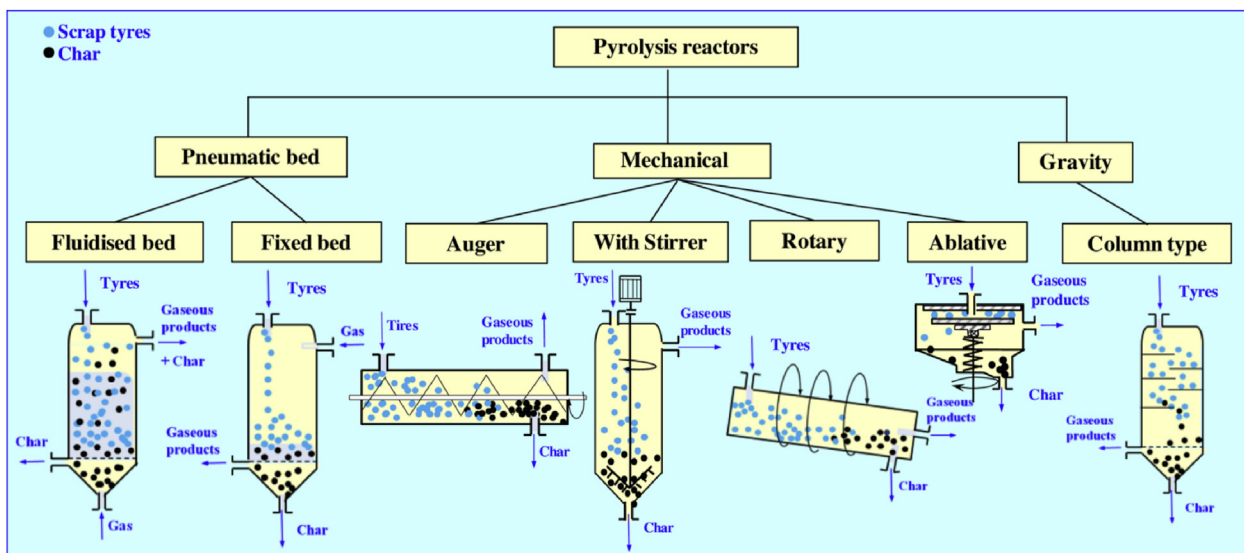|	Fast pyrolysis	Flash pyrolysis	Slow pyrolysis
Temperature (°C)	400−500	800−1000	300−700
Heating rate (°C/s)	10−200	1000	0.1−1
Residence time	30−1500 s	0.5 s	10−100 min

Fig. 10. Types of waste tires pyrolizers [130].

[138]. Paul Williams have published an extensive review about hydrogen and carbon nanotubes formation from bulk plastic waste by catalytic pyrolysis [139].

There are several examples of industrial ventures for plastics valorization. For instance, an industrial process for plastics upcycling to carbon black has been developed by Makeen energy [140]. The process schematic is shown in Fig. 11. The process named 'Plastcon' employs physical and chemical separation of plastics, followed by chemical transformation via pyrolysis. Plastcon is able to process every type of plastic waste from both households and industries. The resulting carbon black has a massive global market, with most of it used to make other plastic materials [140]. Therefore, it is important to consider the full lifecycle of the products to determine the optimal product that can be made in such waste valorization schemes. As shown in Fig. 11, the Plastcon process includes a shredder, which breaks up household plastic waste into smaller pieces. Upon sorting to remove pollutants, such as glass, stone, metal, sand, and other organic materials [140], the densifier is used to heat up the shredded plastic pieces up to an elevated temperature of 200 °C and to melt the mixture into a reduced volume by around 70% [140].

In an anaerobic atmosphere, the pyrolysis reactor vaporises the plastic melt at an elevated temperature of around 400 °C—700 °C. The first product to be deposited is carbon black (about 10% of the plastic waste); this product is used to dye new plastic materials [140]. Condensation is required to separate the various gases from the pyrolysis oil ('crude oil'). The gas (about 15% of the plastic waste) is used to produce heat or power. Pyrolysis oil is the final product, the remaining 75% of the converted plastic waste. This product can be recycled to produce new plastic products. Alternatively, the pyrolysis oil can be processed and refined into 40% naphtha and 60% marine gas oil (MGO). The marine gas oil can be further refined and serve as a low-emission fuel for trucks and ships (although it is still fossil-derived due to the starting material). The produced naphtha can be used to produce plastic materials [140].

If the production of hydrogen can be maximized alongside production of solid carbon high value products that will remain effectively sequestered in durable goods, the upcycling of plastics can serve as a means to produce low emission hydrogen as an energy vector. Furthermore, in terms of solid products, a wide range of carbon materials can be targeted, such as carbon nanotubes, activated carbon, graphene, carbon black [40,134—137,140]. Hydrogen has a broad range of industrial uses and is viewed as a clean fuel that will play an important role in future energy scenarios. Carbon nanotubes have been shown to have unique and favorable features in various applications, and they are recognized as high-value goods. As a result, employing waste plastics as a feedstock to synthesize hydrogen and solid carbon products is a
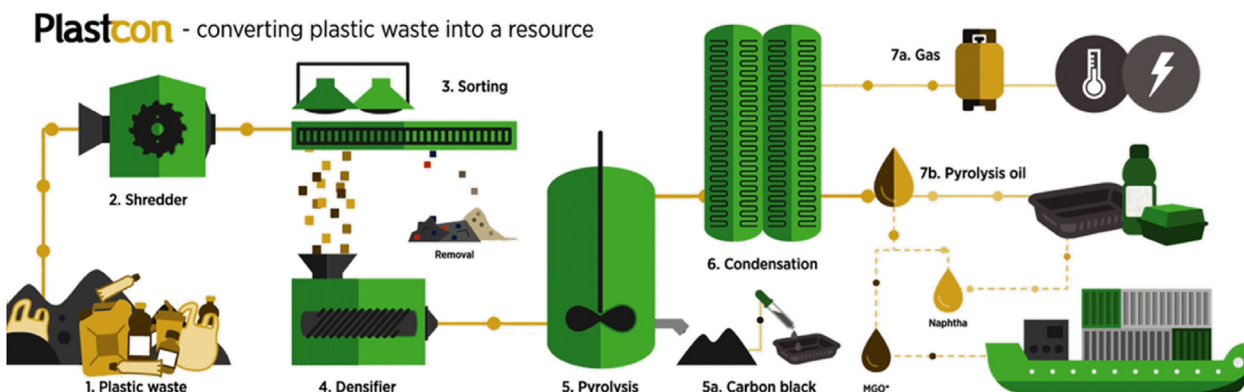

Fig. 11. Schematic diagram of the conversion of plastic waste via pyrolysis, courtesy of Plastcon [140].

promising treatment option. According to published accounts, various reactor designs are employed to create hydrogen and carbon nanomaterials from waste polymers. These studies demonstrate the need for catalyst development to achieve selective production of carbon nanomaterial products and the optimization of operating conditions.

4. Catalyst selection and challenges for thermochemical conversion of plastics

Catalyst development can be an enabler for achieving economically viable thermochemical conversion of plastic. As previously stated, the catalyst should ideally assist in achieving high H_2 production while having a negligible impact on the environment and motivating carbon transformation into carbon nanomaterials, which constitute high value products with growing market size. In this section we identify several catalytic materials and approaches that could be developed further for micro/nanoplastic waste upcycling.

Catalysts can be crucial in increasing thermochemical conversion energy efficiency, stimulating focused reactions, and product selectivity [36]. In general, temperature, residence time, and pressure are all factors that might impact the quality and yield of products. The reaction temperature is a critical parameter. Since the majority of polymers are made of carbon and hydrogen bonds, cleavage of the C−C and C−H bonds needs a significant amount of energy. The temperature has the potential to modify cracking processes, altering the yield and selectivity of gases and liquid oil [36]. These catalysts must be low-cost, stable in heterogeneous mixtures, and highly selective for polymer-to-monomer conversion [141]. Moreover, a proper design of the reactor can also help control the product yield and composition [139,142−145].

Catalysts may be homogenous or heterogeneous. However, homogeneous catalysts are difficult to recover, while heterogeneous catalysts may be separated from liquid mixtures using filtering or centrifugation. As a result, heterogeneous catalysts have received considerable attention for thermochemical upcycling. During catalytic pyrolysis of plastic waste, the porous structure of heterogeneous catalysts performs various functions. The external part of the catalyst achieves thermal cracking, resulting in wax formation. In contrast, the porous interior structure and tiny pore size of the catalyst serve as channels for the selective diffusion and cleavage of larger molecules into smaller ones [146]. The products may be fine-tuned by selecting an appropriate catalyst with modified acidity, pore structure, and shape [126,144]. Acidic catalysts, like zeolites, may be used to decrease the pyrolysis temperature and produce high-quality aromatic, light olefin, and motor fuels [147−149].

Catalytic pyrolysis may be classified into two types: in-situ and ex-situ. In-situ catalytic pyrolysis involves mixing the catalyst and plastic polymers, while ex-situ catalytic pyrolysis involves pyrolyzing the plastic polymers first and then transferring the vapor products to the catalyst bed downstream of the pyrolyzer [150,151]. For in-situ depolymerization, the influence of catalyst structure on depolymerization is important since catalysts come into close contact with the polymer. However, recycling the catalyst in in-situ processes is more complicated. On the other hand, ex-situ mode allows for better temperature control of the pyrolytic and/or catalytic reactions and avoids direct contact between the catalyst and plastic polymers. Thus, ex-situ mode is preferred for large-scale operations, especially when dealing with real-world waste that contains contaminants that might deactivate catalysts [150].

The essential element affecting the final structure of the carbon and selectivity toward desired gas or liquid phase products is the catalyst composition. Because of their high catalytic activity and low cost, heterogeneous Ni-based catalysts are frequently employed. Other kinds of supported catalysts, transition metal-based catalysts, and the addition of a promoter to the catalysts have all been researched to improve CNT and H_2 production [36]. Due to their strong C−C and C−H bond cleavage activity and cheaper cost compared to noble metals, transition metals (Ni, Fe, and Co) have been reported to successfully manufacture H_2 or CNTs from hydrocarbon feedstocks and solid waste [138,152,153]. Catalysts based on nickel are advantageous for thermochemically generating hydrogen from hydrocarbons. For example, using Ni/Al_2O_3 catalysts, a continuous fluidized bed-fixed catalytic bed system has been employed to manufacture CNTs and H_2 [111]. Different calcination atmospheres were used to determine the effect of nickel species distribution on the catalytic activity of the Ni/Al_2O_3 catalyst. At 680 °C, the H-Ni/Al_2O_3 catalyst produced high-quality CNTs (24.3 wt%) with an H_2 yield of 325.4 mmol/g catalyst. Additionally, the combination of carbon black and nickel oxide (Ni_2O_3) was used to convert mixed plastics, which were first catalytically decomposed by carbon black via pyrolysis, yielding aromatics that were then dehydrogenated and reassembled by carbon black and Ni to form carbon nanotubes (CNTs) with a maximum yield of 31.6 wt% [154].

Bimetallic catalysts have attracted interest for their ability to synthesize carbon nanotubes and hydrogen concurrently. For instance, a variety of bimetallic Ni-Mg catalysts that facilitated steam gasification of plastic waste were utilized to increase H_2 production [113,155,156]. Additionally, bimetallic Ni-Fe catalysts have been employed [41,157,158]. A Ni-Fe catalyst and various alumina supports were utilized to transform plastic waste into carbon nanotubes and hydrogen [157]. Due to the homogenous dispersion of the bimetallic Ni-Fe catalyst particles, efficient interaction between metal oxides and the alumina support occurred, enhancing the production of CNTs and H_2. In contrast to Ni-based catalysts, Fe-based catalysts are often utilized to manufacture carbon nanomaterials [152,157]. Catalysts based on Ni, Fe, Co, and Cu have been used to produce carbon nanotubes via the carbon vapor deposition of methane and the thermal conversion of plastic waste. Due to the high carbon solubility of irons, Fe-based catalysts had more CNTs (26.0 wt%) than Ni, Co, and Cu-based catalysts [152].

Multimetallic catalysts have been investigated for the pyrolysis of plastic waste. The Ni−Mg−Al catalyst was utilized to catalyze the pyrolysis−gasification of PP, PS, and HDPE (two-stage system). Ni-Mg-Al significantly enhanced hydrogen generation. Moreover, metallic catalysts such as Ni/γ-Al_2O_3, Ni/α-Al_2O_3, Fe/γ-Al_2O_3, Fe/α-Al_2O_3, and Ni-Fe/γ-Al_2O_3 have been utilized to catalyze the pyrolysis of HDPE, LDPE, PP, and PS to produce oil, hydrogen, and carbon nanotubes [113]. The α-Al_2O_3 supported catalyst had a poorer interaction with metals than the γ-Al_2O_3 supported catalyst, resulting in a larger yield of oil and hydrogen but a lower yield of carbon nanotubes. Compared to Ni, the Fe-based catalyst produced a greater yield of H_2 due to its increased cracking activity. Bimetallic catalysts (e.g., Ni-Fe) can attain a more significant total product yield [157].

Support composition has a significant impact on the activity and stability of catalysts. A good support should have a large surface area and an appropriate pore size or distribution and strong metal-support interaction, mechanical strength, and thermal stability. The most often employed supports are metal oxides, zeolites, and acrylic. Additionally, alumina is an excellent support material due to its strong chemical and mechanical resistance, large surface area, and specific acidic characteristic [159].

While transition metals supported on Al_2O_3 catalysts have been investigated for gasification of polymers, coke deposition may render the catalyst inactive. The acidity of Al_2O_3, in particular, may result in coke deposition on a Ni/Al_2O_3 catalyst. Ni/Al_2O_3 catalysts

promoted with other metals (e.g., Ce, Mg, La, and Zr) have been shown to prevent coke deposition [36].

Numerous Ni-supported catalysts were investigated in an LDPE pyrolysis−steam reforming process for hydrogen generation. Significant impacts on catalytic activity, selectivity, and coke production have been seen with the supports. The most active catalyst in this investigation was Ni/CeO_2, followed by Ni/Al_2O_3 and Ni/Y_2O_3. While these catalysts may aid in the generation of H_2, they may also contribute to the deposition of coke [160]. More information on different supports used for the production of CNTs and H_2 using plastic as feedstock can be found in the literature [36].

Certain compounds included in plastic waste may obstruct catalytic thermochemical conversion processes. Catalysts for the thermochemical conversion of plastic waste should be resistant to air, moisture, and organic pollutants. The development of hydrothermally stable catalysts has been recognized as a research gap because many thermochemical conversions need solvents. Also, the catalysts themselves should be made of a sustainable material. Most catalysts used to convert polymers thermochemically are composed of noble, rare-earth, or transition metals. There is a vital need to make noble and rare-earth-based catalysts reusable and to consider the life cycle of the catalyst used in all cases [161,162].

For supported metal catalysts, sintering of metals is a major issue at elevated operating temperatures, resulting in a considerable loss of active sites/surfaces. This is primarily caused by Ostwald ripening, metal migration, and coalescence. It is proposed that supported metal catalysts should have a high metal dispersion, a homogeneous metal cluster/particle size, and strong metal-support contact to minimize metal mobility and sintering. An additional challenge for catalyst design is to minimize coke formation on the active sites and to target structured carbon nanomaterial formation instead. It has been proposed that the size of metal clusters on the catalysts should be reduced and that metal oxides with a high oxygen capacity (e.g., CeO_2 and ZrO_2) should be introduced to supply oxygen atoms for in-situ burning of coke under plastic conversion conditions to minimize coke formation [163].

5. Challenges of adopting thermochemical technologies to treat micro/nanoplastics

Micro/nanoplastics represent a highly distributed and dilute stream of plastics, which can have a great degree of chemical composition and structure variability based on their source and environmental exposure history. Hence it is unlikely that any one bulk plastic waste conversion method will be optimally suited to treat micro/nanoplastics. However, if micro/nanoplastics can be collected as a feedstock, there could also be benefits from a diminished need to process these particles further mechanically, which can make it easier to transport and chemically process them. This could lead to energy efficiency gains in the upcycling process. While there are significant research needs to develop a viable process for upcycling micro/nanoplastics, it is possible to identify some opportunities based on bulk plastics processing techniques that have previously been explored, in particular keeping in mind the need to shift to products with a lower carbon footprint as well.

6. Products and market opportunities

6.1. The hydrogen rainbow

Hydrogen plays an important role in our current energy landscape, and its use will become increasingly prevalent in the future as an energy carrier. Its application is found in the petrochemical industry, semiconductor industry, as a coolant, energy carrier, and

rocket propellant. All of the thermal conversion techniques used in this research effort for plastic upcycling can generate H_2, although for the most part, chemical upcycling of polymers has focused on producing hydrocarbon products. Devising processes for selective hydrogen production necessitates the development of robust catalysts with stable activity and mechanical integrity under various potential operating conditions and reactor geometries as described in the previous sections. For example, one study demonstrated that non-catalytic hydrothermal carbonization had been found to produce significant amounts of hydrogen gas. The use of marine plastic waste and seawater feed results in various incondensable gases and light hydrocarbons. Fig. 12 illustrates the major gases and light hydrocarbons found at each temperature interval and residence time [35].

As seen from in the figure above, the distribution of gaseous products is diversified with an increase in temperature [35]. Since the feedstock is water pollutants (plastics) that are harmful, repurposing the waste into hydrogen and hydrocarbons makes the use of the process attractive. The study explains that the emitted gases could be combusted. However, methods could be implemented so that the gases could be used as feedstock for other processes. For example, the process could be set as a preliminary process to the production of Methacrolein (due to the great presence of 2-Methyl-1-propene), which is used in the manufacturing of polymers and synthetic resins. Implementation of seawater is also seen as an attractive option as there is a greater supply of seawater than freshwater globally [35].

Presently, due to rising greenhouse gas emissions and the rapid increase in the use of renewable energy sources for power production in recent years, the production of green hydrogen is set to increase massively over the following decades [164]. Hydrogen can be utilized as a storage medium for renewable energy where it would be considered 'green hydrogen'. Green hydrogen can help balance energy production and demand while assisting in decarbonizing the energy system, particularly in transportation and industrial heating applications. The environmental advantages of hydrogen usage depend greatly on the techniques and feedstocks used to produce hydrogen. Therefore, it is critical to establish scalable, low emission hydrogen production technologies to reduce prices and generate hydrogen globally [164].

Hydrogen is mostly generated using the low-cost/high environmental impact steam reforming of methane (SRM) pathway. Because steam reforming of methane is the most established and least expensive industrial technology for hydrogen generation, it produces the majority of hydrogen. Consequently, the global hydrogen production emits 900 Mt of CO_2 each year [165].

Different colors are used to differentiate the various methods of hydrogen production based on the major energy source and level of GHG emissions [164]. At the moment, the majority of hydrogen is gray hydrogen. The gray hydrogen represents hydrogen generated without carbon collection, usage, or storage by steam reforming natural gas or coal (CCUS). Over 40% of gray hydrogen is produced as a by-product of other chemical reactions [166]. The primary drawback of gray hydrogen is the large amount of CO_2 emitted during hydrogen generation [167]. Blue hydrogen is hydrogen generated using steam methane reforming (SRM) with carbon capture and storage. According to Newborough and Cooley [167], a hydrogen-producing plant needs just to install a CCUS device to qualify as blue hydrogen. The precise quantity that must be collected has not been specified. When applied to SRM, up to 90% collection rates were recorded, including postcombustion CO_2 capture [167]. Blue hydrogen is now seen as a bridge technology between green hydrogen and a complete transition to green hydrogen [166]. Green hydrogen is hydrogen produced electrochemically from water using renewable energy sources. This kind of
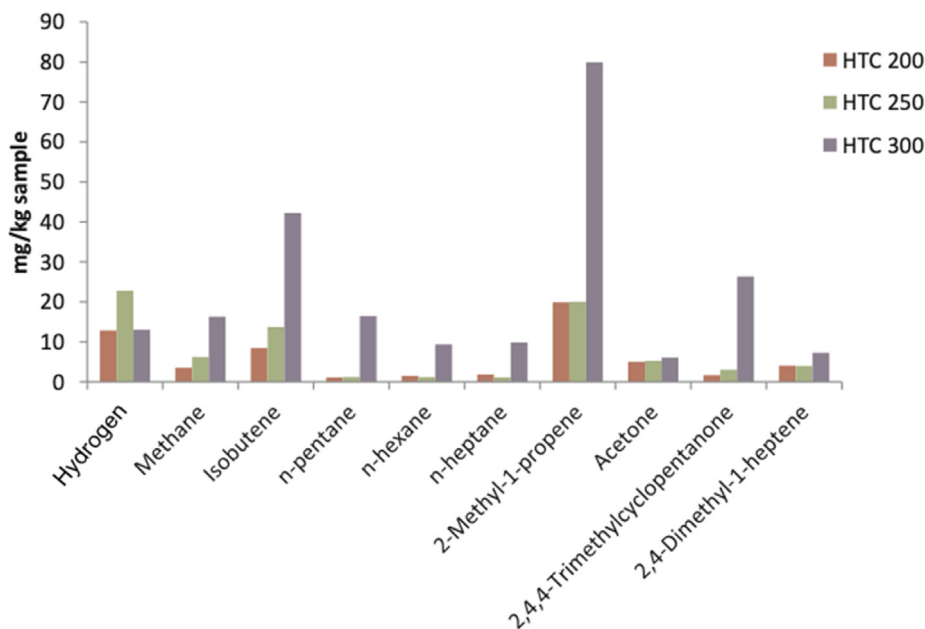
Fig. 12. Distribution of the chemical compounds found in gases of HTC at a temperature of 200 °C(HTC200), 250 °C(HTC250) and 300 °C(HTC300) [35].

hydrogen is particularly valuable as we move to a more sustainable energy and transportation system [168]. While hydrogen generation from nuclear energy is not heavily advocated in European hydrogen programs, it may become a viable option in other parts of the globe, such as China and Russia. This is sometimes called 'purple hydrogen' and is produced electrochemically using electricity generated from nuclear power stations [164].

In contrast to the previously mentioned conventional methods, the by-product of turquoise hydrogen via methane pyrolysis is solid carbon in the form of filamentous carbon or carbon nanotubes. The by-products can be used in subsequent production processes or may be more easily stored, resulting in a lower carbon footprint [169]. Pyrolysis is not yet commercially competitive with SRM in terms of hydrogen generation, but there are examples of large-scale commercial applications when the carbon product is sold as well [170,171]. The hydrogen generated by the technologies studied in the present review can be categorized as turquoise hydrogen if it is generated by thermal decomposition of plastics with most of the carbon ending up in the solid phase. If a low emission energy source can power the process, the carbon emissions related to hydrogen production can be further reduced.

Low-carbon hydrogen generation technologies are essential for a decarbonized economy. Waste valorization techniques should also be developed according to a hydrogen economy vision. This requires more investigation, particularly in developing selective pathways to hydrogen, and presents opportunities for catalyst discovery.

6.2. High-value carbon

Carbon nanomaterials such as CNTs, carbon nanofibers (CNFs) [172], carbon nanosheets (CNS) [173], cup-stacked carbon nanotubes (CS-CNT) [174], and hollow carbon spheres have been created from plastic waste (HCS) [175]. Since their discovery by Iijima, carbon nanotubes (CNTs) have attracted much interest because of their thermal stability, excellent thermal and electrical conductivity, great mechanical strength, high elasticity, excellent tensile strength, flexibility, and semiconducting properties. CNTs have found uses in the automobile sector, where they are employed as

conductive polymers and for plastic reinforcing, as catalytic materials, etc. [176]. Furthermore, CNTs are used as catalyst or catalytic support in various essential scientific disciplines (e.g., energy production and storage, electronics, and medicine) [177]. Chemical vapor deposition of synthetic hydrocarbons is the most popular technique for producing CNTs. Single-step (pyrolysis/gasification), two-step (pyrolysis−reforming or pyrolysis−gasification), and multistep thermochemical processes have been suggested to create CNTs and H_2 from plastic waste [36].

Carbon nanotubes consist of carbon bonded materials, graphene, where carbon atoms are closely organized in an atomic-scale honeycomb (hexagonal) pattern. CNTs are cylinders fabricated of rolled-up graphene sheets [178]. Carbon nanotubes could be synthesized from plastics by applying controlled carbonization process in an oxidizing atmosphere. During this process, the carbonization of plastic occurs in two steps. Initially, there is the degradation of plastics, which is followed by the carbonization of intermediary products with a catalyst. The most important mechanism for the high yield of CNTs is to promote the degradation of plastics to intermediary products such as hydrocarbons and aromatics that are efficient carbon sources. However, this is an emerging area of research with limited knowledge of the growth mechanisms, and yields of CNTs are typically below 10 wt% from carbonization [102].

Carbon nanotubes offer a potentially substantial source of revenue for upcycling schemes. The selling price depends on a few parameters, such as type, purity, and length of the nanotube. A wide range of nanotube sizes (diameter) can be sold; 20 μm, 30 μm, 40 nm, and >50 nm.

Multiwalled carbon nanotubes are priced at above £60.00/g [179]. Single-walled carbon nanotubes are available in two forms: 30 μm with hydroxy functionalization at 90% purity and 20 μm at 95% purity. One gram of these forms of single-walled carbon nanotubes costs £500 [179].

Most established methods to synthesize CNTs employ a vacuum or hydrocarbon process gases at atmospheric pressure. The research work of Takeuchi et al. [180] outlines the various synthesis techniques and the types of CNTs that are produced. The most commonly used CNT synthesis techniques are chemical vapor

deposition, arc discharge, laser ablation, high-pressure carbon monoxide deprotonation, plasma torch, super-growth CVD, liquid electrolysis, and natural, incidental, and controlled flame synthesis [180]. These methods to produce CNTs are energy energy-intensive, non-environmentally friendly due to the gas emissions, and costly. Therefore, the prices of the resulting nanomaterials are very high [181]. Therefore, carbon nanomaterial (CNM) manufacturing methods that are more sustainable and cost-effective are of significant business interest. In this regard, cost-effective and inventive alternative carbon sources, such as plastic waste might be very appealing [136].

Chemical vapor deposition (CVD) is the dominant mode for the production of CNTs worldwide [41]. The catalytic vapor phase deposition of carbon was first discovered in 1952. However, the actual synthesis of CNTs was developed in 1993, and in 2007, researchers developed the process to grow CNTs that grew to an impressive 18 mm. The growth of carbon nanotubes on alumina-supported nickel catalyst via thermal CVD was studied by Dikonimos Makris in 2005 [182]. Commercially, alumina-supported nickel catalysts are used to reform methane, but there is a method that can use these catalysts to produce a large number of carbon nanotubes. Various parameters that encourage growth, such as time, temperature, pressure, and concentration, were tested by Th. Dikonimos Makris and co-workers, and these were optimized for maximum carbon yield [182].

Effect of growth time on carbon amount and growth rate formed at constant temperature (600 °C), pressure (100 mbar), and $H_2/CH_4 = 10/70$ ratio were studied. The carbon yield is maximized as the growth time is extended. However, the growth rate reduces over time due to the limited catalyst distribution on the surface [182]. Another factor that affects the growth rate involves the nucleation time of the nanotubes, i.e., some of the CNTs nucleate at a fast rate and are still expanding in length, while other CNTs start to nucleate. According to Gong and co-authors, based on high-pressure carbonization, 80 (weight percentage) wt% CNT yield with diameters ranging between 20 and 60 nm could be achieved [102].

Continuous production of CNTs has been found in employing 2 stage pyrolysis–gasification reactors loaded with nickel-based catalysts. This method produced hydrogen as a co-product and CNTs with diameters ranging from 10 to 20 nm. In contrast, the yield was far lower as the two-stage method only managed to yield CNTs of less than 20 °C. Lastly, a pyrolysis–combustion–carbonization method was found to produce CNTs that were 30–100 nm in outer diameter and 30 μm long. Therefore, not only does the method determine the overall quality of the CNTs, other factors such as the type of catalyst, composition of feed, and type of feed determine the yield and growth of CNTs during production [102].

Several important factors contribute to the final morphology of the carbon produced in this process. Liu YF et al. (2003), have discovered that the ratio between toluene and benzene in the carbon source has an important influence on the carbon nanotube morphology. Straight carbon nanotubes are more prevalent (compared to curled nanotubes) when pure benzene is used as the carbon source and the number of curled nanotubes increases as the amount of toluene in the carbon source increases [183]. While mixed bulk plastics are a difficult and highly variable feedstock for conversion to high purity CNTs of a certain type, there are some wastes, such as synthetic textiles, that may provide a more consistent supply of hydrocarbons (through the thermochemical transformations outlined herein) to be able to synthesize higher value nanostructured carbons.

It is worth mentioning that other types of carbon materials can also be produced with the technologies analyzed in this review. Graphite is made up of carbon layers (with covalent and metallic bonding inside each layer) and layers connected by a weak van der Waals interaction. Graphene layers are the carbon layers of graphite. Graphite is anisotropic, having excellent electrical and thermal conductivity inside the layers (owing to in plane metallic bonding) and low electrical and thermal conductivity perpendicular to the layers (due to the weak Van Der Waals forces between the layers) [184]. The market price of high purity graphite powder is around US $15.00–10.00/kg. Due to graphite utilization as lithium batteries component, this price has steadily increased in time with increasing demand [185]. Moreover, Carbon fibers have a crystallographic pattern that aligns carbon layers parallel to the fiber axis, even if the layers themselves are not flat. For lightweight constructions, carbon fibers have often utilized as a reinforcement in polymer-matrix composites [184]. Amorphous carbon has comparable bonding and structure to graphite, but without long-range order. The degree of crystallinity of amorphous carbon increases with heating (called degree of graphitization). Numerous carbons utilized in practice, such as carbon fibers, are not completely graphitic but have a broad range of graphitization degrees, depending on the temperature of heat treatment. Therefore, amorphous carbon can be utilized as an intermediate product to produce CNTs or graphite [184].

7. Conclusion, challenges, and future work

Each of the technologies that have been described herein has its advantages and drawbacks. However, plastics waste conversion also presents broader challenges that need to be overcome before wide-scale implementation. It is known that 8 million tons (Mt) of plastic waste reaches the ocean each year [24]. This amount of plastic is estimated to be triple by 2040 [4]. In addition, plastic has to be collected from the environment and processed. Hence, the scale-up of thermochemical conversion technologies is vital to ensure the circular economy of plastic and micro/nanoplastics. The main challenge is the high cost and time demand of the collection of plastic wastes once they have made their way into the environment. Furthermore, it is necessary to develop more thorough methods that allow the collection of micro/nanoplastics from the aquatic environment, such as those released in vast quantities from washing machines.

Micro/nanoplastics collection methods (i.e., those applicable to washing machines) are not able to separate different kinds of plastics (i.e., nylon vs. polyester). They are likely to result in a variable composition waste, containing household contaminants. This can present a challenge for catalytic upcycling methods since micro/nanoplastics collected may contain some contaminants and non-polymer species that can poison and deactivate the catalyst. The reactor design and process optimization will become essential for managing the variability of feedstocks. There are opportunities to leverage the know-how developed for biomass valorization, especially in discovering durable catalysts and developing processes for handling wet solid feedstock. Micro/nanoplastics in water present a potentially highly variable reactant that includes some biomass (such as organic fibers from cotton, for example). The transport cost from the collection point to the processing plant has also to be considered as this is a distributed source of hydrocarbons.

Among thermochemical upcycling techniques, gasification and pyrolysis are promising for large-scale applications. Liquefaction and HTC are efficient in producing oil products but present high costs due to the need for high pressures and the utilization of different solvents. Regarding gasification and pyrolysis, there are opportunities to target hydrogen and solid carbon product formation that result in sequestration of the carbon (rather than contributing to increasing GHG emissions) alongside low emission fuels (i.e., hydrogen) production. The use of a catalyst can enable

greater selectivity toward desired products. Computational chemistry offers a broad toolkit for investigating the mechanistic aspects of catalytic processes and can produce practical solutions to allow rational catalyst design through first-principles approaches. Recent advances in automated systems for reaction path analysis present an opportunity for removing human bias from computational catalysis investigations, leading to potentially faster, more effectively guided experimental efforts [186].

The primary barrier to commercialization is the catalytic thermochemical conversion technologies' cost-competitiveness in a no incentive scenario where the products have to compete with fossil fuel-derived alternatives. Numerous thermochemical conversion technologies may be unable to compete with established petrochemical corporations without substantial subsidies for two reasons: (1) the generated oil has poor economic value, and (2) sorting the mixed feedstock is costly.

It is necessary to minimize plastics consumption through a cultural change while also finding technologies to complete the loop by recycling and substituting to accomplish a long-term shift in the system. Our suggested solutions may be used to minimize leakage into the environment by producing high-value goods, although they alone will not be sufficient for sustainability. It is also essential to completely change the way we produce plastics for end uses that consider them a necessity. Designing biodegradable plastics and new pathways for circular use are crucial aspects of ensuring sustainability. Bioplastic innovation is one way to prevent harmful effects of waste leakage to the environment.

When evaluating upcycling techniques for existing plastics waste, it is essential to consider the entire life cycle of products, particularly to target products that do not result in oxidation of the carbon contained in plastics to CO_2. The plastics and climate change issues are interlinked due to the use of fossil-derived carbon in plastics. Thus, it is essential to focus on waste management and valorization technologies that do not simply shift the carbon to the gas phase, thus contributing to climate change. For micro/nanoplastics waste, upcycling to carbon nanomaterials and green energy vectors can be a suitable and sustainable solution since the product downstream use is not expected to contribute to increasing GHG emissions. Moreover, the currently high prices for some carbon nanomaterial products can incentivize the collection and utilization of plastic waste. Due to the global scale of the problem and the rapid pace at which we need progress, ambitious collaboration efforts (i.e., between basic scientific research, engineering development, industries, governments, and computational studies) are needed to accelerate research, develop, and optimize promising processes and create viable solutions for a circular economy.

Author contribution

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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