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Advances in the pyrolysis of end-of-life tires: A critical review of reactor systems, process conditions and industrial applications

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ABSTRACT

The growing environmental concerns and increasing volumes of end-of-life tires (ELT) have driven global interest in sustainable recycling solutions. Pyrolysis has emerged as a promising thermochemical process for converting waste tires into valuable materials, including tire pyrolysis oil (TPO), gas, and recovered carbon black. This review presents a comprehensive analysis of scientific literature and patents, focusing on reactor technologies, operating conditions, and innovations that influence product distribution and quality. The study explores key parameters – temperature, pressure, particle size, and residence time – highlighting their impact on pyrolysis efficiency and the characteristics of the resulting products. Particular attention is given to reactor design advancements, including fixed-bed, fluidized-bed, auger, rotary kiln, and stirred systems, as well as patent-driven innovations in heat transfer, mixing, and energy integration. Challenges related to the variability and quality of recovered carbon black and its integration into new tire manufacturing are critically assessed, with emphasis on the need for process optimization and post-treatment strategies to meet industrial carbon black standards and support circular tire manufacturing.

1. Introduction

1.1. Management of end-of-life tires

Global tire production reached approximately 2.3 billion units in 2022 and in 2028 is estimated to reach 2.7 billion units, leading to a significant number of end-of-life tires (ELT) being generated [1]. In 2019, the worldwide generation of ELT totaled 30.9 million tons and after their lifecycle, these tires can either be recycled or disposed of [2]. However, due to the non-biodegradable nature of tires and the associated risks such as soil and water contamination, fire hazards, and other environmental concerns, landfilling of ELT has been largely abandoned and reprocessing strategies have been adopted [3–5].

This review is particularly timely, as both industrial and policy-driven efforts to promote sustainable tire recycling are gaining momentum. In Europe, nearly 95 % of ELT are now treated through material or energy recovery, driven by regulatory frameworks aligned with the EU Green Deal and the Circular Economy Action Plan [2,6]. These policies have significantly reduced the number of tires in landfills from 78 %, in 1994, to only 5 % by 2019. Globally, ELT management practices differ, with roughly 40 % of tires ending up in landfills, 42 % used for material recovery, and 15 % for energy recovery [2].

Tires are primarily composed of natural rubber and styrene-butadiene rubber (41–45 %), steel (13–15 %), carbon black (about 28 %), polymer fibers, and inorganic compounds (14–17 %), which include antioxidants and accelerators like sulfur, zinc oxide, and silica [7,8]. Currently, material recycling of ELT is performed by specialized companies that mechanically extract steel and textiles and produce rubber crumb [9]. The rubber crumb is widely used in various applications, such as synthetic turf, recreational surfaces, molded products, asphalt, and civil engineering [10]. Despite these uses, there are growing concerns regarding its application in synthetic turf, due to the potential release of volatile and carcinogenic compounds like polycyclic aromatic hydrocarbons (PAH) and its contribution to microplastic pollution [11]. As a result, discussions are underway to implement legislation that could prohibit the use of rubber crumb in this sector [12]. Additionally, the

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high calorific value of tires (~32 MJ kg^{-1}) makes them suitable for energy recovery through incineration, however this process emits pollutants and does not recover reusable materials [13]. Tire retreading offers an alternative, reducing material consumption and CO_2 emissions, although the final product may be of lower quality [14]. While traditional material and energy recovery techniques can be used to repurpose ELT, the complex composition of tires calls for more effective solutions, such as pyrolysis, which offers significant potential for ELT valorization by enabling both material and energy recovery within the framework of a circular economy [8].

1.2. Pyrolysis of end-of-life tires

Pyrolysis is a thermochemical process that decomposes ELT into valuable products, including tire pyrolysis oil (TPO), gas, and char by heating the material in the absence of oxygen [10], as shown in Fig. 1. Operating at high temperatures, typically between 300 °C and 800 °C, pyrolysis breaks down the complex polymeric structures of natural and synthetic rubbers found in tires, resulting in smaller hydrocarbon molecules [15]. The heating process triggers a series of volatilization and decomposition reactions, such as dehydration, cracking, isomerization, dehydrogenation, aromatization, and condensation, which together determine the final product distribution [16]. Typically, the solid fraction (char) accounts for 35–40 wt% of the total products from ELT pyrolysis, the liquid fraction (TPO) yield ranges from 35 to 45 wt% and the gas fraction accounts for 10–30 wt% [10]. These yields are influenced not only by the reactor design and operating conditions, but also by the composition of the feedstock.

The pyrolysis gas product is predominantly composed of light hydrocarbons (C_1–C_4), hydrogen and minor amounts of sulfur- and nitrogen-containing volatile compounds [17]. Specifically, the gas phase typically contains hydrogen (H_2), methane (CH_4), ethane (C_2H_6), ethene (C_2H_4), propane (C_3H_8), propene (C_3H_6), butane (C_4H_{10}), butene (C_4H_8), butadiene (C_4H_6), carbon dioxide (CO_2), carbon monoxide (CO) and hydrogen sulfide (H_2S) [18].

This gas mixture exhibits a significant calorific value, reported to range from approximately 20 MJ·m^{-3} to over 65 MJ·m^{-3} [18]. The wide variation in energy content is primarily attributed to differences in the gas composition, which in turn depend on several key factors, such as pyrolysis temperature, heating rate and reactor type. This gas can be utilized to meet the energy demands of the industrial process, it can be burned to provide heat for the pyrolysis itself or used in downstream applications, making it an attractive by-product for integrated energy recovery systems [17].

Tire pyrolysis oil, derived from the volatile fraction of ELT pyrolysis, is a dark opaque liquid with a pungent odor [19]. It is a highly complex mixture containing over 100 different compounds, which can be refined into various fuel fractions, including gasoline (C_5–C_{10}), diesel (C_{14}–C_{18}), and heavy oil (>C_{18}) [20]. The chemical composition of TPO consists of aliphatic hydrocarbons, aromatic hydrocarbons, heteroatoms, and polar components [18]. Among these, aromatic hydrocarbons constitute a significant proportion, approximately 62.4 %, and include compounds such as benzene, toluene, xylene, styrene, limonene, and PAH [20]. Aliphatic hydrocarbons make up around 31.6 % and primarily consist of alkanes and olefins, with straight-chain hydrocarbons ranging from C_6 to C_{37} [18,20].

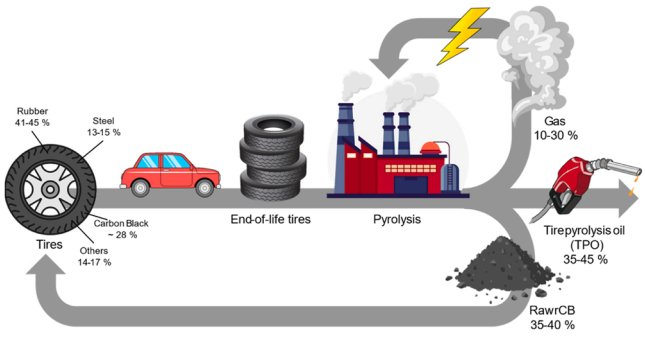


Fig. 1. Schematic representation of the ELT pyrolysis process, highlighting the decomposition of rubber components into tire pyrolysis oil, gas, and raw rCB.

Despite its potential as an alternative fuel source, TPO possesses several unfavorable properties that limit its direct use in engines [17]. It is highly acidic, has a high sulfur content, and exhibits low thermal stability. Additionally, its viscosity and flash point make it unsuitable for direct combustion. The sulfur content of TPO typically ranges from 1 to 2 wt%, significantly higher than that of commercial diesel, which is below 0.05 wt% [20]. Consequently, further refining processes such as hydrogenation, desulfurization, or catalytic treatment are necessary to enhance its quality [20]. Once treated, TPO can be blended with conventional diesel or other fuels to meet industry standards, making it a viable substitute for fossil fuels [17]. Moreover, it can serve as a high-calorific fuel for large-scale combustion equipment, such as boilers and heating furnaces, highlighting its potential as a sustainable energy source [20].

The solid product (char) obtained from the pyrolysis of ELT, known as raw recovered carbon black (raw rCB), is a complex mixture resulting from the compounds used in tires manufacturing. Raw rCB is composed primarily of carbon black (CB), inorganic contaminants, trace amounts of steel and carbonaceous residues. The inorganic contaminants, which make up 10–20 wt%, consist of additives and fillers such as zinc oxide, silicon oxide, and calcium carbonate, commonly used in the rubber formulations [10,18]. The carbonaceous residues are disorganized carbon deposits formed during the pyrolysis process due to secondary reactions like repolymerization, and they are estimated to account for around 4 wt% of the total solid product [10,21]. Additionally, raw rCB exhibits some degree of organic contamination due to volatile molecules that tend to adsorb onto its surface or become trapped within its pores [21]. These compounds are formed during the thermal degradation of rubber polymers and include aliphatic and aromatic hydrocarbons, such as olefins, heteroaromatics, and PAH.

The primary objective of producing rCB – which refers to the raw rCB obtained after milling – is to partially or fully substitute commercial CB, particularly semi-reinforcing grades such as CB N660. To extend its use toward replacing reinforcing grades like CB N330, it is essential that the rCB exhibits chemical composition and morphological characteristics comparable to those of conventional commercial CB.

1.3. Carbon black

Carbon black is a finely particulate solid composed of amorphous carbon, being produced through the partial combustion or thermal decomposition of fossil fuels such as natural gas, petroleum, and coal oil [21]. The production of CB in the industry typically uses six conventional methods: furnace black, lampblack, channel black, gas black, acetylene black, and thermal black [22]. These methods are categorized based on the type of chemical process involved – either thermal-oxidative decomposition or thermal decomposition – and whether the decomposition occurs in an open or closed system [23]. Furnace black, lampblack, and channel black are generated through the incomplete combustion of hydrocarbons in the presence of air (thermal-oxidative decomposition), while thermal black and acetylene black are produced by thermal decomposition of hydrocarbons in oxygen-free environments [23]. Further details on these production methods can be found in the Supplementary Material.

The exact mechanism behind CB particle formation remains a subject of debate, although several theories have been proposed. Despite ongoing discussions, it is widely accepted that CB formation follows a process like soot formation, where hydrocarbon-based feedstocks decompose into carbon, hydrogen, and oxygen radicals (if oxygen is present) [24]. The formation of PAH is a crucial precursor step, as these

compounds facilitate the slow conversion of aliphatic molecules into aromatic structures, which eventually develop into CB particles [23,24]. This process can be broken down into five sequential stages, that are represented in Fig. 2.

The first stage involves the pyrolysis of hydrocarbon feedstock under intense heat, leading to the formation of PAH. This process involves the dehydrogenation of hydrocarbon molecules into atomic carbon and ions, which then condense into semisolid carbon precursors [23]. In the second stage, the nucleation process begins, where large PAH molecules transition from a gaseous to a particulate state, forming initial CB nuclei. The third stage sees the growth and aggregation of these particles as they collide and coalesce into larger structures, gradually shifting from spherical shapes to fractal geometries [23,25]. The fourth stage is characterized by further surface growth, where small molecules attach to existing CB particles, forming aggregates with a layered microstructure [26]. Finally, the oxidation stage occurs, either concurrently or subsequently, depending on the flame type, as oxidation competes with CB formation. Various factors, including temperature, oxygen concentration, and fuel composition, influence this oxidation process [23].

CB is primarily composed of carbon (97–99 wt%), with smaller quantities of other elements, including oxygen, hydrogen, nitrogen, sulfur, and trace amounts of metals, which originate either from the feedstock or from additives used in the production process [23]. The composition and structure of CB make it a vital industrial material, widely used across various sectors for its reinforcing, pigmentation, and conductivity properties.

The properties of CB, including particle size, surface area, structure, and surface chemistry, can be tailored to meet the needs of specific industrial applications. The material's classification follows an ASTM standard [27], which assigns grades based on a code consisting of a letter and three digits (*e.g.*, Nxxx or Sxxx). The letter refers to CB structure (N – Standard; S – Low) and the first digit corresponds to particle size and surface area, while the remaining digits are arbitrary identifiers. Table 1 summarizes the ASTM classification of CB grades.

CB is indispensable in the rubber industry, particularly in tire manufacturing, where it serves as a reinforcing filler. Approximately 90 % of CB is used in rubber products to enhance properties such as tensile strength, abrasion resistance, and durability [28]. In addition to its primary role in rubber reinforcement, CB is also widely employed as a pigment in black, bluish, brown, and gray colorants. Its electrical conductivity makes it suitable as a filler in coatings, inks, and batteries. CB also acts as a UV stabilizer in polymers and is used in paints and inks to adjust viscosity [29].

The performance of CB in different applications is significantly influenced by its surface area and structure. For instance, higher surface area CB, such as N110 and N220, offers superior reinforcement, making it ideal for high-stress applications like off-road tires, where enhanced abrasion resistance and tear strength are critical [21]. In contrast, grades with lower surface area, such as N550 and N660, provide moderate reinforcement with reduced emphasis on elongation and fatigue resistance, making them better suited for applications like tire liners and hoses [21]. CB grades with extremely low surface area and structure, such as N990, are tailored for applications where reinforcement is less important but excellent thermal and electrical insulation properties are required, such as wire insulation, gaskets, and O-rings [21].

Table 1
ASTM classification of carbon black grades, where the first digit denotes the particle size range and corresponding surface area. Adapted from [10].

First Digit (ASTM grade)	Particle Size (nm)	Surface Area ($m^2\ g^{-1}$)
0	0–10	> 150
1	11–19	121–150
2	20–25	100–120
3	26–30	70–99
4	31–39	50–69
5	40–48	40–49
6	49–60	33–39
7	61–100	21–32
8	101–200	11–20
9	201–500	0–10

1.4. Recovered carbon black

The market relevance of rCB has grown significantly in recent years as shown in Fig. 3. The global rCB market was valued at USD 259.3 million in 2024 and is projected to reach USD 706.5 million by 2030, with an estimated compound annual growth rate (CAGR) of 16.4 % between 2025 and 2030. This rapid growth is driven by increasing demand in tire manufacturing – which accounted for over 70 % of market share as of 2024 – as well as in rubber goods, plastics, and coatings, as well as stricter environmental regulations supporting circular economy initiatives.

Leading tire manufacturers have set ambitious sustainability targets, aiming to incorporate 40 % rCB in new tires by 2030 and achieve full replacement of commercial CB with rCB by 2050. However, realizing these goals requires a deep understanding of the fundamental differences between commercial CB and rCB, and of the impact of rCB structure, reinforcing ability, and overall performance in rubber

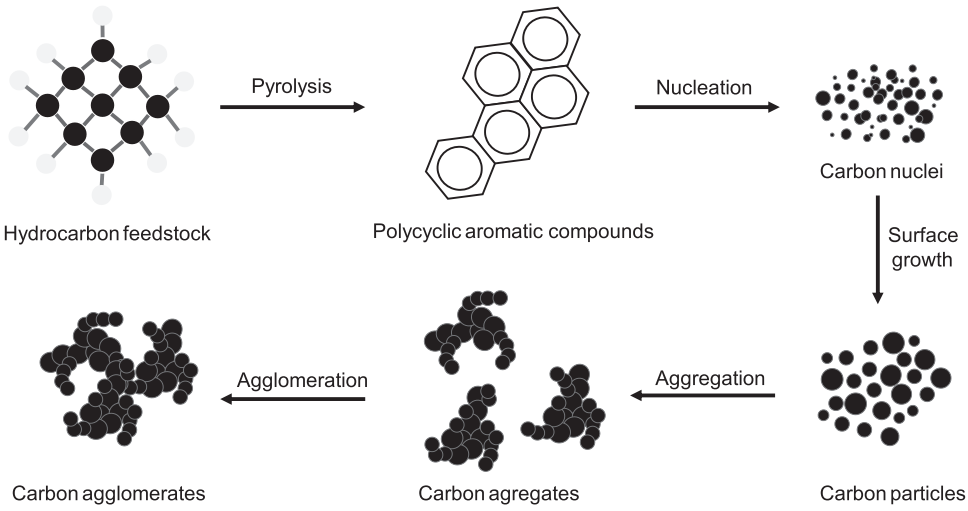


Fig. 2. Proposed mechanism of carbon black formation from hydrocarbon feedstocks, outlining the key stages: pyrolysis, nucleation, surface growth, aggregation, and agglomeration.

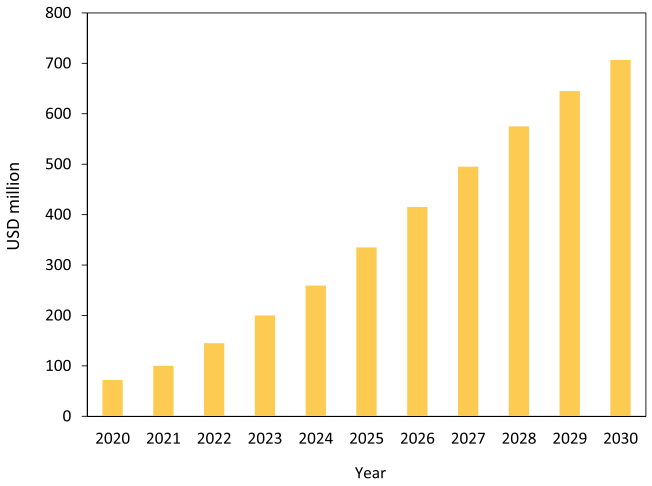


Fig. 3. Projected global market size (USD million) of recovered carbon black (rCB) from 2020 to 2030. Adapted from [30].

matrices. Unlike commercial CB, rCB contains large amounts of inorganic impurities, has lower surface area, and exhibits a different particle morphology, which can affect its dispersion and reinforcement properties in rubber applications. Successfully integrating rCB into tire formulations will depend on advancements in pyrolysis technology and post-processing techniques to enhance rCB quality, consistency, and reinforcing properties.

There are several standardized methods to assess rCB properties, as outlined in Table 2, which provide crucial insights into its composition, surface characteristics, and performance attributes. Beyond these methods, the reinforcing potential of rCB is often evaluated through its application in rubber compounds, followed by mechanical and dynamic testing of the resulting materials. Such performance-based assessments provide a practical understanding of how rCB behaves in real-world formulations. Silva *et al.* [31] conducted a comprehensive review of the literature on the mechanical behavior of rubber compounds containing rCB produced via pyrolysis, highlighting key findings and remaining challenges in this field.

Table 2
Standardized test methods used to characterize recovered carbon black (rCB), namely the ASTM procedures for assessing chemical composition, surface area, contamination, morphology, and mechanical properties relevant to tire and rubber applications [32].

Properties	Test method	ASTM
Proximate analysis	Thermogravimetric analysis	ASTM D8474
Sulfur	High-temperature combustion with infrared absorption detection procedures	ASTM D1619
Ash content	Calcination	ASTM D1506
Organic contamination	Toluene transmittance	ASTM D1618
PAH determination	Soxhlet extraction and gas chromatography with mass spectrometry	ASTM D8143
Benzo-α-Pyrene content	Soxhlet extraction and gas chromatography with mass spectrometry	ASTM D7771
Morphological characterization	Scanning electron microscopy	ASTM D3849
Surface area	Brunauer–Emmett–Teller (BET) theory	ASTM D6556
Heating loss	Mass loss	ASTM D1509
Pour density	Measuring the mass of rCB in a known volume	ASTM D1513
pH value	Digital pH meter	ASTM D1512
Dispersion in rubber	Agglomerate count with light microscope	ASTM D2663
Sieve residue	Wire-mesh screen of a specified size	ASTM D1514
Pellet fines and attrition	Sieving	ASTM D1508
Pellet size distribution	Sieving	ASTM D1511
Pellet mass strength	Mass strength tester with hollow compression cylinder and plunger	ASTM D1937
Automated individual pellet hardness	Automated pellet hardness tester	ASTM D5230

Achieving full-scale replacement of CB with rCB requires, above all, an in-depth understanding of how tire pyrolysis conditions influence the yield and properties of the pyrolysis products. Additionally, economic feasibility and environmental sustainability must be thoroughly evaluated to ensure that rCB production can serve as a viable alternative to conventional CB manufacturing. Therefore, optimizing pyrolysis conditions should not only focus on maximizing product yield and quality but also integrate life cycle assessment (LCA) and cost analysis to assess its long-term viability as a sustainable industrial solution.

This review examines existing literature, including both academic articles and patents, on the pyrolysis of ELT, focusing on equipment types, operating parameters, and optimized conditions. For the literature review, a targeted query was conducted in Scopus using the search terms: TITLE: pyrolysis AND (waste OR end-of-life) AND (tires OR tyres). The search results indicate a total of 709 articles and 52 patents published between 1974 and 2025. Fig. 4 illustrates the temporal evolution of research in this field, highlighting the growing interest and advancements in ELT pyrolysis technology over the years. A notable increase in publications – particularly in academic research – began in the early 2000s, with exponential growth since then. This trend reflects growing interest in ELT pyrolysis, driven by environmental concerns, the demand for sustainable waste management solutions, and advancements in pyrolysis technology. However, the comparatively lower number of patents suggests a lag in the transition from research to industrial application, emphasizing the need for further innovation, process optimization, and commercialization efforts to bridge this gap and fully integrate pyrolysis technology into sustainable circular economy models.

An extensive literature review on the pyrolysis of ELT, covering articles published between 2015 and 2025, is available in the Supplementary Material.

2. Pyrolysis system and operating conditions

As mentioned before, pyrolysis is a thermochemical process that comprises several reactions to produce hydrocarbon-rich liquids and gases, as well as solid carbon products. The efficiency and output of pyrolysis depend heavily on several key factors, including temperature, pressure, particle size, residence time and reactor type [15]. Each one of these parameters significantly influence the yield and composition of pyrolysis products, impacting the balance between liquid, gas, and solid products.

2.1. Pyrolysis mechanism

Despite extensive research, the exact pyrolysis mechanism of tires remains incompletely understood due to the complex decomposition behavior of their components. While some studies have focused only the pyrolysis mechanism based on natural rubber (NR) decomposition, [33] others have attempted to incorporate the major polymers present in tires, such as NR, butadiene rubber (BR) and styrene-butadiene rubber (SBR), to provide a more comprehensive understanding of the process [34,35]. During the pyrolysis process, rubber components volatilize, generating gaseous and liquid products, while carbon materials convert into char [15]. Meanwhile, non-carbon elements – including hydrogen, nitrogen, and sulfur – are released, affecting the porosity of the resulting char. Han *et al.* [36] studied the pyrolysis mechanism of waste tires and

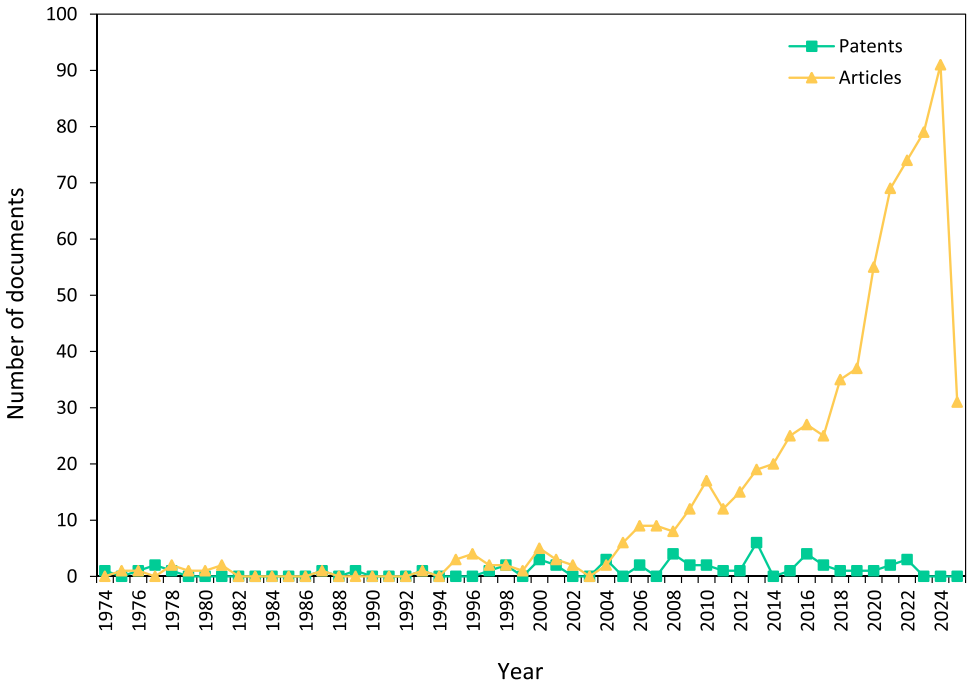


Fig. 4. Temporal evolution of the number of articles and patents on ELT pyrolysis, from 1974 to 2025, indicating rising academic and industrial interest in the field. Literature search performed in Scopus with the words "pyrolysis" AND "waste OR end-of-life" AND "tyres OR tires" in the TITLE (01/04/2025).

found that tire pyrolysis occurs in four distinct stages, each characterized by specific decomposition reactions. The first stage, occurring between 200 and 350 °C involves water vaporization and the decomposition of the volatile compounds in rubbers, such as oil, plasticizers and additives. The second stage, between 300 and 450 °C, is primarily attributed to the decomposition of NR. The third stage, around 400–500 °C, corresponds to the degradation of SBR and BR components. For temperatures above 520 °C only minimal weight loss is observed, indicating limited further decomposition.

Key reactions in pyrolysis encompass depolymerization, sublimation, and polymerization. Depolymerization includes chain scission, end-chain scission, and chain stripping, breaking long carbon chains into smaller molecules [37]. Sublimation drives phase transitions (*e.g.*, solid to gas), while polymerization in the final stages results in cross-linking and coke formation [37]. Initially, long carbon chains break down, releasing carbon and hydrogen molecules. These molecules rearrange and cross-link, forming various hydrocarbons in liquid and gas phases [15]. The primary gaseous products include alkanes, alkenes, hydrogen, carbon monoxide, and carbon dioxide [34]. Key alkenes, such as 2-pentene, 1,3-butadiene, and isoprene, originate from NR and SBR, while cyclic alkenes (*e.g.*, D-limonene, 5-methyl-1,3-cyclopentadiene, and 1-methyl-1,4-cyclohexadiene) and aromatic compounds (*e.g.*, benzene, toluene, xylene, and styrene) are formed through secondary reactions [34,35,38]

A more comprehensive pyrolysis mechanism of NR, BR and SBR was proposed by Li *et al.* [35] based on Thermogravimetry – Fourier Transform Infrared Spectroscopy/Mass Spectrometry (TG – FTIR/MS) and Pyrolysis – Gas Chromatography – Time-of-flight Mass Spectrometry (Py – GC – TOF/MS) analysis. NR undergoes thermal cracking through two primary pathways to form free radicals at elevated temperatures. In one pathway free radicals form conjugated systems that further generate isoprene, while in another pathway radicals rearrange and cyclize to form D-limonene [35]. Simultaneously, Diels-Alder reactions convert isoprene into D-limonene, illustrating the complex thermal degradation of NR, as shown in Fig. 5a). The pyrolysis of BR follows four distinct transformation pathways. Initially, scission and dehydrogenation lead to the formation of 1,3-butadienes. Simultaneously, free radicals undergo rearrangement and cyclization, producing 4-vinyl-1-cyclohexenes. Another pathway involves dehydrogenation and cyclization, forming 1,3-cyclopentadienes, while a parallel cyclization process leads to the formation of 1,4-cycloheptadienes [35]. These complex thermal cracking mechanisms of BR are illustrated in Fig. 5b). The pyrolysis of SBR forms free radicals at higher temperatures, with radicals containing C_4 chains forming primarily 1,3-butadienes, while benzene-derived free radicals produce styrene. Additionally, other reactions could occur forming benzene, xylene, and other benzene derivatives [35]. The pyrolysis pathway of SBR under hyperthermic and anoxic conditions is detailed in Fig. 5c).

2.2. Reactor type

Pyrolysis reactors play a crucial role in enabling the controlled thermal decomposition of raw materials under high temperatures, varying pressures, and oxygen-free conditions, often with the presence of inert or fluidized gases. Different reactor types are employed to optimize the production of oil, char, or gas, depending on process requirements. Pyrolysis reactors are primarily classified based on feedstock movement within the system. In stationary reactors the feedstock remains fixed, while in dynamic reactors it is moved by pneumatic forces (as seen in fluidized, spouted, circulating, and vortex reactors) or mechanical forces (such as in auger, stirrer, ablative, screw, centrifuge, and rotary reactors) [15].

2.2.1. Fixed bed reactor

Fixed bed reactors are widely used in laboratory-scale pyrolysis studies of waste tires due to their simplicity, ease of operation, and cost-effectiveness. These reactors typically operate in semi-continuous mode, where the feedstock remains stationary while being gradually heated in an inert atmosphere to prevent combustion [39]. The pyrolysis process in lab-scale fixed bed reactors occurs within a quartz tube, with temperatures typically ranging between 300 °C and 700 °C [15]. As the waste tires decompose, the volatile compounds are purged from the reactor by an inert gas (*e.g.*, nitrogen), as illustrated in Fig. 6, then pass through a condenser to form liquid pyrolysis oil, while the remaining

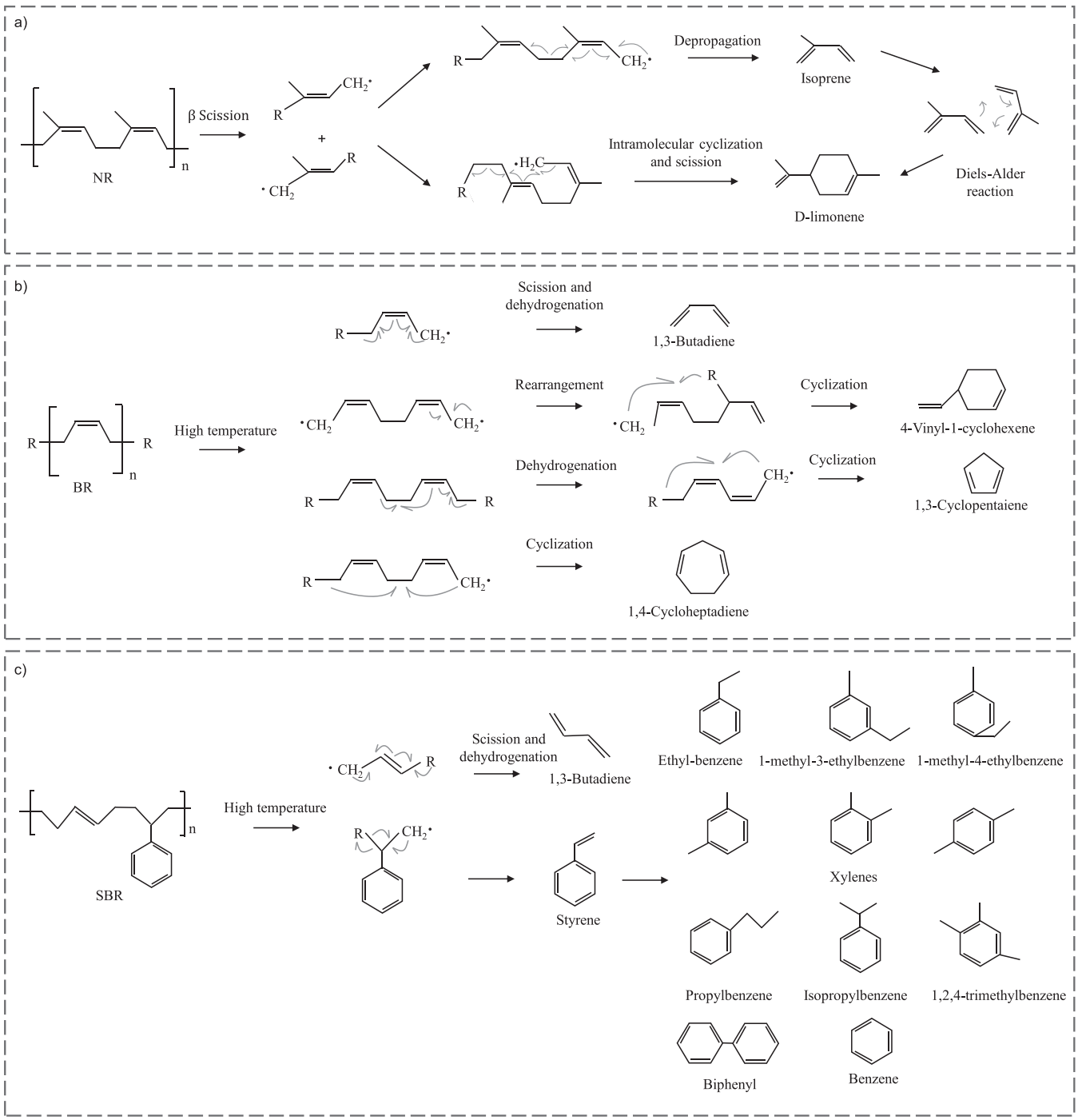


Fig. 5. Proposed thermal degradation mechanisms of the three main rubber polymers in tires: (a) Natural rubber (NR), (b) Butadiene rubber (BR), and (c) Styrene-butadiene rubber (SBR), as identified through spectroscopic and mass spectrometry analysis. Adapted from [34,35].

solid residue is collected at the bottom of the reactor [39].

Fixed bed reactors can be categorized into several configurations, including vertical fixed bed reactors, horizontal fixed bed reactors, and catalytic fixed bed reactors [39]. Each configuration offers specific advantages. Vertical and horizontal fixed bed reactors efficiently handle different feedstock sizes and shapes without segregation concerns, while catalytic fixed bed reactors improve product yield and selectivity by facilitating catalytic cracking and reducing unwanted secondary reactions [39]. Additionally, these reactors can also be loaded with heat carriers (*e.g.*, steel shot, ceramic balls, sand) to ensure uniform heat transfer and improved temperature control.

One of the key benefits of fixed bed reactors is the minimal back-mixing of feedstock, leading to more predictable product distribution [40]. Despite their advantages, fixed bed reactors also present challenges. The semi-batch operation mode limits their scalability to commercial applications, making them more suitable for preliminary research. The relatively slow heat transfer rate can lead to non-uniform heating and lower conversion efficiency. Another drawback is the difficulty of removing tar and char residues from the reactor, which can lead to operational inefficiencies and maintenance issues [15].

Several studies have analyzed the effect of fixed-bed operating parameters such as temperature, heating rate, and particle size on pyrolysis product yield and quality [41–45]. For example, Taleb *et al.* [43] investigated the effects of temperature (300–700 °C), feedstock particle

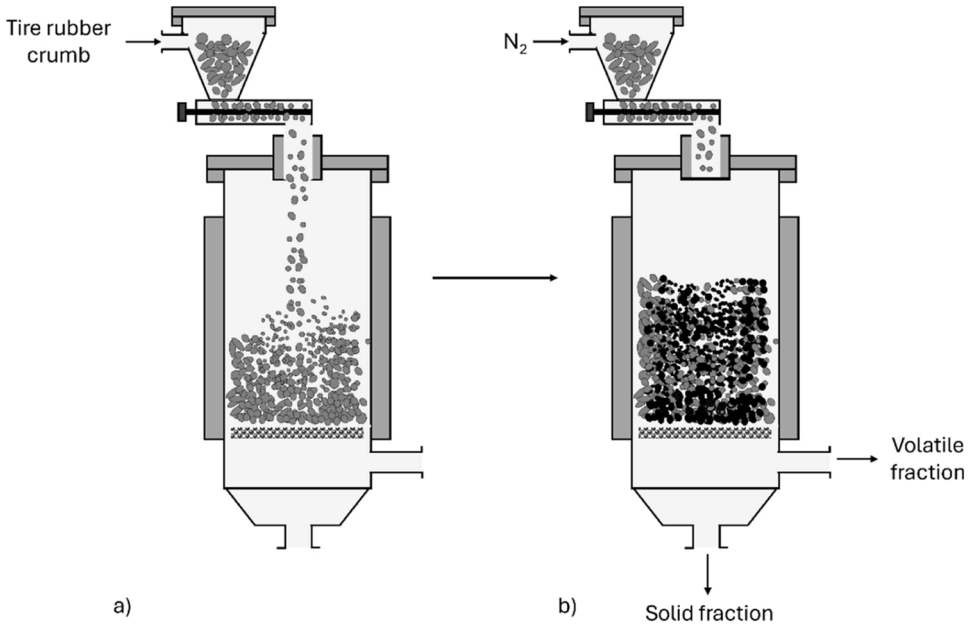


Fig. 6. Configuration of a typical fixed-bed reactor used in pyrolysis of waste tires, illustrating the feedstock placement (a), and the pyrolysis process (b).

size (80, 40 and 18 mesh) and carrier gas flow rate (1 and 5 min^{-1}) on the pyrolysis of waste tire in a lab-scale fixed bed reactor. Their findings revealed that liquid yield increased with temperature, reaching a peak at 500 °C before declining, while char yield decreased from 300 °C to 500 °C and then stabilized. Meanwhile, the gas yield consistently increased from 300 °C to 700 °C, indicating a shift toward gas production at higher temperatures. Higher carrier gas flow rates increase the superficial gas velocity, which reduces vapor residence time in the fixed bed, minimizing secondary reactions of pyrolysis volatiles, which would decrease the yield of gaseous products or aromatic compounds. Under optimal conditions (500 °C, 80-mesh particle size, and 5 min^{-1} inert gas flow rate) the oil yield reached 32 wt% [43], demonstrating the importance of fine-tuning process parameters for maximizing products recovery.

The use of catalytic beds enhances the efficiency of fixed bed reactors. Catalytic beds can increase the specific surface area of tire char and reduce sulfur content in the pyrolysis oil [46]. Depending on the design, the catalyst bed can be placed directly above the tire waste, allowing contact with both the carbonaceous solid surface and the primary pyrolysis vapors. In this configuration, cracking reactions occur via both homogeneous (solid–solid) and heterogeneous (vapor–solid) pathways [47]. Alternatively, the catalyst bed can be positioned at mid-height within the reactor, where only pyrolysis vapors come into contact with the catalyst, facilitating cracking exclusively through heterogeneous reactions [47]. For instance, Kordoghli *et al.* [48] studied the influence of the number of fixed catalyst beds (0, 1, or 2) on the pyrolysis of ELT. Their results showed that the presence of catalysts influenced the yield of pyrolysis products, with char yields ranging from 36 to 43 wt%, liquid yields from 24 to 34 wt%, and gas yields from 22 to 30 wt%, depending on the catalyst type and number of catalytic beds. These findings highlight the role of catalysts in improving product selectivity and optimizing pyrolysis performance.

In conclusion, fixed bed reactors remain a widely used and cost-effective option for laboratory-scale pyrolysis of waste tires, providing process flexibility and enabling studies on various feedstock compositions and reaction conditions. Their simple design and predictable product distribution make them well-suited for experimental research and catalyst testing. However, scalability challenges, slow heat transfer, and residue accumulation limit their feasibility for large-scale industrial applications.

2.2.2. *Fluidized bed reactor*

Fluidized bed reactors, illustrated in Fig. 7, have gained significant attention in the pyrolysis of ELT due to their continuous mode of operation, high heat transfer efficiency, and fast pyrolysis conditions [39]. In a fluidized bed reactor, a gas or liquid is introduced from the bottom of the reactor creating a suspended state of movement for the solid particles, which promotes efficient mixing and uniform heat distribution [15]. These reactors come in several configurations, including bubbling fluidized beds, spouted beds, and circulating fluidized beds [15]. While they differ in design, particularly in the method of how the fluidizing gas is introduced and the relative gas to liquid flow, they all share the advantage of maintaining a uniform temperature along the bed and enabling fast pyrolysis conditions.

A fluidized bed reactor typically consists of several key components, including the freeboard, fluidization area, sieve bottom, cyclone separator, and quench cooler [15]. The freeboard is a large open area above the fluidization surface where solid particles disengage from the gas phase. The fluidization area facilitates the movement of the feedstock in

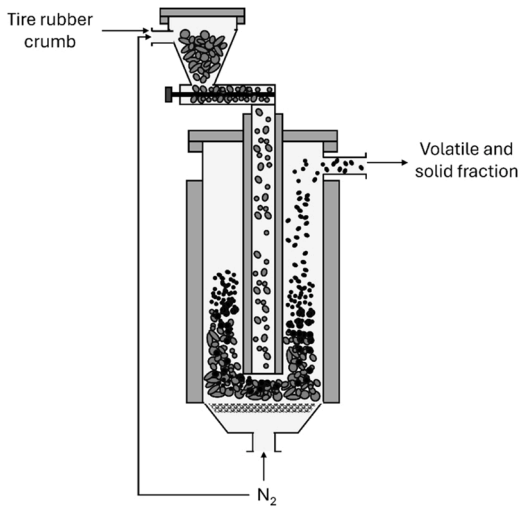


Fig. 7. Fluidized bed reactor system showing the feedstock feed and the fluidization zone, designed to enable efficient heat and mass transfer.

the presence of a fluidizing gas. The sieve bottom consists of multiple or single nozzles that regulate the inert gas flow, ensuring a superficial velocity that keeps particles suspended without excessive entrainment. The cyclone separator removes char particles, while the quench cooler condenses pyrolysis volatiles into oil and gas fractions.

Fluidized bed reactors remain a preferred choice for tire pyrolysis due to their high heat and mass transfer rates, uniform temperature distribution, continuous processing capability and flexibility in catalyst use [39]. The high heat transfer efficiency of fluidized beds allows for short residence times, which helps reduce secondary reactions, improving product selectivity and oil yield [39]. Fluidized bed reactors are particularly advantageous for industrial applications, where consistent product quality and scalability are essential for economic viability. Despite these advantages, limited axial temperature control within the bed can lead to temperature variations, which may affect product uniformity [15]. Furthermore, high energy consumption, high investment costs, and long cooling times due to high gas throughput pose economic and operational challenges [39]. The requirement for small feedstock particle sizes (0.1–2.0 mm) is another limitation, as larger particles require more energy for fluidization thus can reduce process efficiency [15,39]. Additionally, tire char produced in fluidized bed reactors tend to have a smaller specific surface area and fewer pores compared to char formed in fixed bed reactors, primarily due to the shorter residence time [39]. Moreover, issues like particle agglomeration and sintering at lower temperatures can disrupt fluidization and impact reactor performance [49].

The efficiency of fluidized bed pyrolysis is significantly influenced by feedstock characteristics and process parameters, such as particle size, feed rate, and temperature. Dai et al. [50] investigated the impact of temperature, residence time and particle size on pyrolysis product distribution. They found that increasing the pyrolysis temperature from 360 to 450 °C led to a decrease in char yield, from 40 wt% to 27 wt%, while in the range 450–810 °C char yields remained almost constant at 32 wt%. They also observed that when residence time increased from 1 to 5 s, at 500 °C, both oil and char yields decreased while gas yield increased slightly. Particle size played a significant role in pyrolysis efficiency with the 0.8 mm sample producing higher char yields, and lower gas and oil yields, compared to the 0.32 mm sample. This occurs because larger particle sizes reduce heating rates and favor carbonization, while smaller particle sizes provided a greater reaction surface area, promoting char reduction and leading to higher gas production [50]. Further studies on char properties obtained in fluidized bed reactors revealed that increasing pyrolysis temperature from 500 to 600 °C improved char quality and purity [51]. In fact, this temperature rise increased the specific surface area of tire char, from 73 to 85 $m^2\ g^{-1}$, reduced its sulfur content, from 2.3 to 2.1 wt%, and decreased its ash content, from 11.3 to 10.6 wt% [51].

In conclusion, fluidized bed reactors are among the most efficient and widely used technologies for continuous waste tire pyrolysis, offering high oil yield, excellent heat transfer, and fast reaction times. Their ability to operate under fast pyrolysis conditions makes them highly suitable for large-scale applications. However, temperature control, high energy consumption, and particle agglomeration remain key challenges that must be addressed to improve process efficiency.

2.2.3. Auger reactor

Auger type reactors, illustrated in Fig. 8, represent a significant innovation in pyrolysis technology, with improved heat transfer efficiency and shorter residence times for solid materials when compared to fixed-bed reactors [39]. These reactors utilize a rotating helical screw, similar to those used to transport solid materials in industry, to move rubber feedstock through a heated, oxygen-free chamber, ensuring continuous processing and controlled residence time [15]. The residence time of solids within the reactor is regulated by adjusting the screw's rotational speed and the space between screw flights. Their design enhances heat transfer, promotes uniform particle mixing, and improves

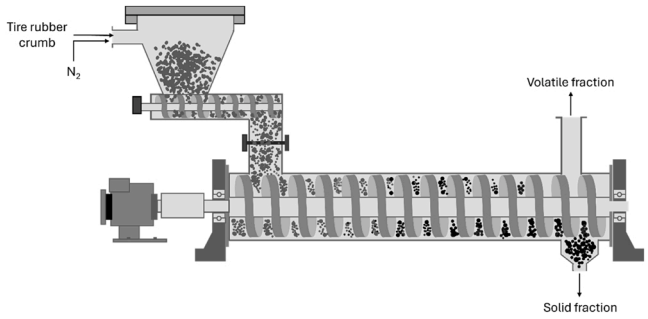


Fig. 8. Single-screw auger reactor layout used for continuous pyrolysis, showing the helical transport mechanism.

contact between the feedstock and the heated wall, which are critical for efficient pyrolysis [52]. Auger reactors are particularly versatile, supporting both slow pyrolysis, which favors char production, and fast pyrolysis, aimed at maximizing oil yield. This adaptability makes them suitable for processing a wide range of feedstocks, including ELT, biomass, municipal solid waste and plastics [52].

Auger reactors are available in two primary configurations: single-screw and twin-screw reactors. Single-screw reactors rely primarily on external heating via reactor walls, whereas twin-screw reactors can achieve better feedstock mixing and incorporate the feed of granular heat carriers (*e.g.*, hot sand or steel balls), which improve direct heat transfer, thermal efficiency, and product consistency [52].

In tire pyrolysis, twin-auger reactors generally yield more tire char compared to single-auger systems [39]. However, tire char from twin-auger reactors tends to have lower heating value, volatile matter content, and BET surface area than that from single-auger reactors. From a tire char perspective, twin-auger reactors outperform single-auger systems, as they enhance feedstock mixing, prevent material accumulation, and reduce the risk of clogging [39]. Additionally, the twin-screw mechanism ensures a steady feed rate and improves interaction between particles, particularly when granular heat carriers are used. Furthermore, twin-screw designs require less mechanical energy to operate, making them more cost-effective and reliable for continuous pyrolysis applications [52].

Despite the several advantages offered by auger reactors, there are some drawbacks. Compared to fluidized bed and ablative reactors, they have a longer residence time for pyrolysis vapors, which can cause unwanted secondary reactions that affect product quality [15,39]. Preventing material clogging and achieving effective mixing in the radial direction is difficult, often requiring specialized screw flight designs to optimize particle distribution and heat exposure [52]. Furthermore, large-size or irregularly shaped feedstocks can lead to accumulation and clogging [39,52]. Addressing these challenges is essential for improving reactor performance and enabling successful large-scale applications.

The distribution of pyrolysis products in auger reactors is strongly influenced by operating conditions. Martínez et al. [53] studied the pyrolysis of waste tires in a pilot scale auger reactor to obtain reliable data for potential process scale-up. Their experiments were conducted under optimized conditions, selected to maximize liquid yield and tire rubber conversion, namely at 550 °C and atmospheric pressure, using N_2 as carrier gas with a flow rate of 5 min^{-1}, and a waste tire mass flow rate of 6.7 h^{-1}. The feedstock residence time was fixed at 3 min by adjusting the screw rotation speed. Pyrolysis was performed for over 100 h, demonstrating excellent reproducibility and process stability with average product yields of 42.6 wt% for liquid, 40.5 wt% for solid (raw rCB), and 16.9 wt% for gas [53]. Further research by Martínez *et al.* [54] investigated the impact of temperature, waste tire mass flow rate, solid residence time, and N_2 volumetric flow rate on product yields in a twin-screw auger reactor. Their results revealed that temperature and feedstock mass flow rate had the most significant statistical influence on pyrolysis product distribution. They also optimized the operating

conditions to maximize liquid yield, achieving oil, raw rCB, and gas yields of 45, 40, and 15 wt%, respectively. These optimal results were obtained when the reactor was operated at 475 °C, with a feed rate of 1.5 h^{-1}, a residence time of 3.5 min, and an N_2 flow rate of 0.1 min^{-1}, highlighting the importance of process parameter optimization for efficient pyrolysis performance.

In conclusion, auger reactors are a promising technology for waste tire pyrolysis, offering continuous operation, efficient heat transfer, and process flexibility. Their compact design and ease of scalability make them suitable for industrial applications, while their ability to accommodate various feedstock increases their potential for waste valorization. However, challenges such as feedstock clogging, extended vapor residence times, and difficulties in radial mixing must be addressed to enhance process efficiency. Further advancements in screw design, temperature control, and material handling could improve the overall performance of auger reactors and facilitate their widespread industrial adoption for sustainable waste-to-energy solutions.

2.2.4. Rotary kiln reactor

The rotary kiln reactor, illustrated in Fig. 9, is a widely used technology for the pyrolysis of waste tires due to its ability to process feedstocks of varying shapes and sizes [55]. It consists of an inclined cylindrical drum with a rotating shaft, lined with refractory material to withstand high temperatures [56]. The continuous rotation of the drum enhances mass transfer and heat transfer, ensuring better mixing of the feedstock during pyrolysis process [57]. In continuous operation, shredded tires are fed through the upper end of the reactor, while char is collected from the lower end.

The key advantages of rotary kiln reactors include their adaptability to processing different sizes and shapes of waste tires, good control over process variables like residence time, and suitability for continuous feed operations [55]. The residence time in these systems is controlled by the angle of the drum and its rotation speed [57]. Nonetheless, rotary kilns also face several challenges, including uneven temperature distribution, significant heat loss and high energy consumption [39,58]. Additionally, char produced in this type of reactor tends to contain higher levels of volatile matter, ash, and sulfur due to incomplete pyrolysis and temperature fluctuations [39].

Several studies have analyzed the performance of rotary kiln reactors in tire pyrolysis. Yazdani *et al.* [59] conducted pyrolysis experiments under a nitrogen atmosphere, with temperatures ranging from 400 to 1050 °C. Their results showed that higher temperatures increased gas yield while reducing char yield, with the highest oil yield (44 wt%) obtained at 550 °C. Similarly, Galvagno *et al.* [60] performed pyrolysis in a pilot-scale rotary kiln, varying the process temperature between 550 and 680 °C. Their results showed that as the temperature increased, the char yield decreased slightly, from 49.09 wt% to 48.86 wt%, while oil yield decreased from 38.12 wt% to 31.82 wt%. In contrast, gas yield significantly increased, from 2.39 wt% to 10.75 wt%, demonstrating the shift towards higher gas production at high temperatures. These findings highlight the critical role of temperature in optimizing product distribution.

In conclusion, rotary kiln reactors remain a prominent choice for waste tire pyrolysis due to their continuous processing capability, flexibility in handling different feedstock sizes, and effective mixing of materials. However, challenges such as heat loss, uneven temperature distribution, and char contamination must be addressed to improve efficiency and product quality.

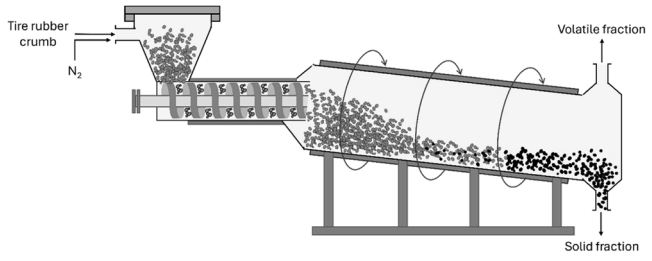


Fig. 9. Rotary kiln reactor setup for waste tire pyrolysis, illustrating inclined rotating drum design and the continuous feeding system.

2.2.5. Stirred tank reactor

Stirred reactors, illustrated in Fig. 10, utilize mechanical agitation to ensure uniform mixing and heat distribution throughout the feedstock. These reactors consist of a cylindrical vessel equipped with an internal stirring mechanism, such as impellers or paddles.

The mechanical agitation in stirred reactors ensures that the feedstock particles are consistently exposed to heat, reducing temperature gradients and promoting efficient thermal decomposition [61]. This feature is particularly useful for handling heterogeneous or viscous feedstocks, such as biomass, plastic waste, and end-of-life tires.

One of the primary advantages of stirred reactors is their ability to enhance mass and heat transfer. Continuous mixing minimizes the formation of hot spots and prevents incomplete pyrolysis, leading to more uniform product yields. Additionally, agitation helps to reduce coking and fouling reactions by preventing the buildup of char on the reactor walls, which extends the operational life of the reactor. The flexibility of stirred reactors makes them suitable for catalytic pyrolysis, where catalysts can be added to improve product quality and enhance the cracking of complex hydrocarbons. Despite their advantages, stirred reactors present some challenges, including higher energy consumption, due to the mechanical agitation, and potential wear and tear of moving parts exposed to high temperatures and abrasive materials. Additionally, while stirred reactors are effective for laboratory and pilot-scale studies, scaling up to industrial applications can be complex. Nevertheless, their ability to handle diverse feedstocks and maintain consistent pyrolysis conditions makes stirred reactors a valuable option for both research and potential industrial-scale pyrolysis processes.

Li *et al.* [62] investigated the effect of temperature on pyrolysis product yields in a continuously stirred batch reactor. Their study revealed that when temperature increased from 430 to 500 °C the gas yield decreased from 8.00 wt% to 4.50 wt%. The highest char yield (48.67 wt%) was observed for pyrolysis at 430 °C and declined to 40.0 wt% when the temperature increased to 470 °C, remaining practically constant for temperatures above 470 °C. The oil yield exhibited a significant increase with rising temperatures, being 43.3 wt% at 430 °C, reaching 53.5 wt% at 470 °C, and further increasing to 55.5 wt% at

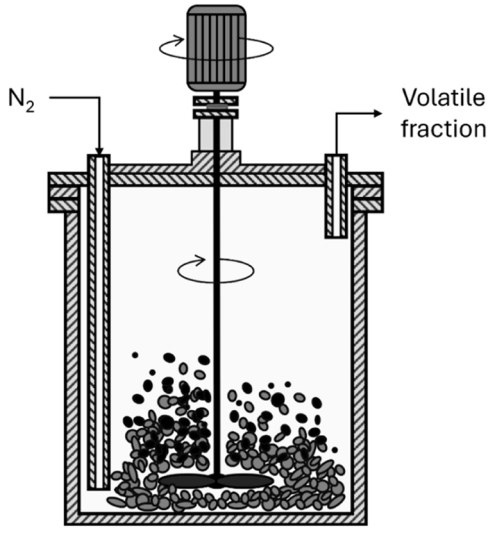


Fig. 10. Stirred reactor configuration highlighting mechanical agitation of feedstock, which enhances mixing, heat distribution, and temperature control during pyrolysis.

500 °C. The optimal pyrolysis temperature for maximizing the oil yield was 500 °C, where the gas, oil, and char yields were 4.50 wt%, 55.5 wt %, and 40.0 wt%, respectively. These findings highlight the importance of temperature control in optimizing pyrolysis efficiency.

In conclusion, stirred reactors play a crucial role in enhancing pyrolysis efficiency by ensuring uniform heat distribution, reducing temperature gradients, and improving mass transfer. Their mechanical agitation minimizes char buildup and optimizes residence time, making them particularly effective for catalytic pyrolysis. However, challenges such as high energy consumption and mechanical wear remain barriers to large-scale application.

To facilitate a clearer comparison among reactor types, Table 3 summarizes their key advantages and limitations with respect to thermal efficiency, scalability, product selectivity, and suitability under various process conditions.

The ternary diagram (Fig. 11) presents the distribution of pyrolysis products – char, oil, and gas – obtained from the pyrolysis of waste tires using different reactor types, including fixed-bed, auger, circulating spouted bed reactor (CSBR), and rotary kiln. Each data point represents the product composition in weight percentage (wt%), with colors distinguishing the reactor type. The data for this analysis were collected from scientific literature published between 2015 and 2025, providing a comprehensive overview of experimental results from various studies.

Fixed-bed reactors (blue symbol in Fig. 11) are the most used in laboratory-scale pyrolysis experiments due to their simplicity, ease of operation, and cost-effectiveness. The diagram shows that auger (red symbol), rotary kiln (purple symbol), and CSBR (green symbol) reactors exhibit a similar distribution of pyrolysis products. Contrarily, the distribution of pyrolysis products is more dispersed in fixed bed reactors due to the wider ranges of temperature and residence times tested in this type of equipment.

Table 3
Comparative analysis of common reactor types used in waste tire pyrolysis, summarizing their main advantages, disadvantages, and operational features.

Reactor	Advantages	Disadvantages
Fixed bed	– Available in several configurations – Simple design – Low cost – Enables studies on various feedstocks and reaction conditions – Minimal back-mixing of feedstock	– Limited scalability – Slow heat transfer – Residue accumulation
Fluidized bed	– High heat and mass transfer rates – Continuous processing capability – Short residence times – Suitable for large-scale applications	– High energy consumption – Difficult axial temperature control – Requires feedstocks with small particle sizes – High investment costs – Risk of particle agglomeration
Auger	– Efficient heat transfer – Good control of residence time – Short residence times for solids – Promotes uniform particle mixing – Process flexibility – Compact design – Easy scalability – Accommodates various feedstocks – Supports both slow and fast pyrolysis	– Longer residence time for pyrolysis vapors – Risk of material clogging – Limitations in radial mixing
Rotary kiln	– Continuous processing capability – Flexibility in handling different feedstock sizes – Effective mixing of materials – Good control over process variables like residence time	– Hight heat losses – Uneven temperature distribution – High energy consumption
Stirred tank	– Uniform heat distribution – Reduced temperature gradients – Improves mass transfer – Minimum char buildup	– High energy consumption – High mechanical wear – Difficult to scale-up

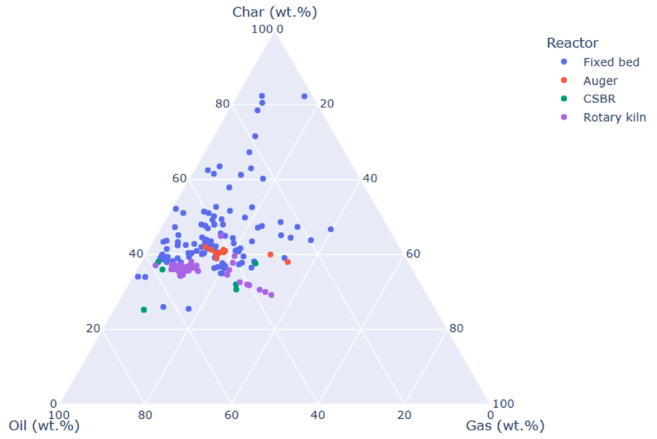


Fig. 11. Ternary diagram showing the distribution of pyrolysis products (char, oil, and gas) yields across different reactor types (fixed-bed, auger, rotary kiln, CSBR), based on experimental data from the literature published between 2015 and 2025.

2.3. Temperature

Numerous studies have demonstrated that the yield of pyrolysis products (oil, gas, and char) is highly dependent on the operating temperature of the pyrolysis process [63–69]. According to Zerin *et al.* [15], the typical ranges for char, oil, and gas yields are 30–50 wt%, 30–65 wt % and 0–30 wt%, respectively. At lower temperatures, oil production is favored, while at higher temperatures, the process shifts toward the generation of gas, and char yields tend to stabilize [15]. Ramani *et al.* [68] examined the effect of temperature on product distribution and found that the yield of pyrolysis oil declined from around 35 wt% at 500 °C to below 20 wt% at 750 °C. In contrast, the yield of pyrolysis gas rose significantly, from about 25 wt% at 500 °C to over 45 wt% at 750 °C. These variations are driven by the different cracking reactions that occur at varying temperatures, with more intense cracking leading to lighter products such as gases, and milder cracking favoring the production of heavier liquid products. Moreover, temperature not only impacts product yields but also their composition, as reactions such as cracking, cyclization, and aromatization dominate at specific temperature ranges.

At lower temperatures, typically below 400 °C, the pyrolysis process remains incomplete, inducing only mild cracking reactions. While the thermal energy is sufficient to break down polymeric chains into heavier hydrocarbons, it is insufficient for the full decomposition of these large molecules. Rodriguez *et al.* [13] conducted pyrolysis of ELT at 300 °C and 400 °C, concluding that the process was incomplete at both these temperatures. Their findings showed solid yields of 87.6 wt% and 55.9 wt%, respectively – significantly higher than theoretical expectations. Additionally, raw rCB exhibited a heterogeneous, sticky, and gummy appearance, indicating the presence of residual polymeric materials, further confirming that pyrolysis was not fully achieved.

In the temperature range between 450 °C and 600 °C, cracking reactions become more pronounced. The increased thermal energy allows for more extensive breakdown of larger hydrocarbon molecules, resulting in a mix of liquid and gaseous products [15]. At these temperatures, the cracking reactions are sufficiently intense to produce pyrolysis oils, while still avoiding excessive fragmentation into gases. The temperature range between 500 °C and 600 °C is often identified as optimal for maximizing oil production: Yazdani *et al.* [59] achieved the highest oil yield of 44 wt% at 550 °C, Berrueco *et al.* [70] identified 500 °C as the optimal temperature for maximizing oil production, reaching a

yield of approximately 40 wt%.

As the pyrolysis temperature increases, secondary reactions such as cyclization, dehydrogenation, and aromatization occur more rapidly, leading to a reduction in aliphatic components and an increase in aromatic compounds in the pyrolysis oil, such as limonene, benzene, toluene, and xylene [20]. Wang *et al.* [67] reported that increasing the pyrolysis temperature from 350 °C to 500 °C significantly increased the aromatic hydrocarbon content in TPO, while decreasing the portion of aliphatic hydrocarbons. Similarly, Williams *et al.* [71] found that when the pyrolysis temperature increased from 450 °C to 600 °C, the aromatic content increased, and the aliphatic content decreased. Zhang *et al.* [66] further noted that below 750 K, elevated temperatures intensified intramolecular hydrogen transfer in limonene, promoting its isomerization and the formation of alkenes. However, above 750 K, higher temperatures favored the transformation of limonene into monocyclic aromatic hydrocarbons. Supporting these findings on an industrial-scale, Sanchís *et al.* [72] demonstrated that pyrolyzing truck tires and passenger car tires at temperatures between 425 °C and 775 °C led to increased synthesis of aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes in the liquid phase. These findings confirm the significant impact of temperature on the composition of pyrolysis products.

At temperatures exceeding 600 °C, cracking reactions become significantly more intense, resulting in the predominance of gas production over liquid yields. The increased thermal energy drives secondary cracking reactions, breaking down intermediate hydrocarbons into smaller volatile gases such as methane, hydrogen, and carbon monoxide [15]. Aylón *et al.* [73] observed that when temperatures rise from 600 °C to 800 °C, liquid yields decrease (from 45.5 wt% to 27.5 wt %) and gas production increases (from 17.9 wt% to 31.5 wt%), reflecting a shift toward more extensive cracking at higher temperatures.

The char yield remains relatively stable at temperatures above 500 °C, typically ranging from 35 wt% to 45 wt% [74]. Li *et al.* [75] studied the pyrolysis of scrap tires in a rotary kiln reactor at temperatures between 500 °C and 600 °C, demonstrating that temperature had minimal effect on raw rCB yield, with 41.3 wt% at 500 °C and 39.3 wt% at 600 °C. Similarly, Aylón *et al.* [73] reported that solid yields remained constant in the range 600 °C to 800 °C, fluctuating between 39 wt% and 41 wt%. This stability in char yield is attributed to the near-complete decomposition of volatile components at higher temperatures, leaving behind a carbon-rich residue. However, at temperatures below 500 °C, the char produced during pyrolysis tends to have limited pore development, resulting in incomplete pyrolysis [39]. This leads to a higher char yield but with lower quality, as pyrolysis volatiles can adhere to the char's surface. As temperatures rise, the quality of the char improves with a notable reduction in volatile content and enhancements in surface area and porosity, making it more suitable for high-value applications, such as energy storage, adsorption, and as a reinforcing agent [39]. Galvagno *et al.* [60] confirmed this trend, reporting a decrease in volatile content from 12.78 wt% at 550 °C to 5.24 wt% at 680 °C. Similarly, Li *et al.* [75] observed a significant reduction in volatile content, from 16.14 wt% at 500 °C to 5.86 wt% at 600 °C, further highlighting the impact of temperature on char properties. However, at excessively high temperatures the char can experience sintering, which reduces the volume of micropores and mesopores, decreases the specific surface area, and negatively impacts the surface properties of the material [39]. These temperature-dependent structural changes significantly influence the quality and potential applications of the char.

López *et al.* [76] conducted the pyrolysis of scrap tires in a conical spouted bed reactor within the 425–600 °C temperature range. Fig. 12 illustrates the evolution of pyrolysis product yields across the studied temperatures, summarizing the variation trends of different fractions as a function of temperature. The gas yield increases with temperature, which is consistent with the expected thermal cracking behavior, where higher temperatures promote secondary cracking of heavier hydrocarbons into gaseous products. In contrast, the tar fraction remains

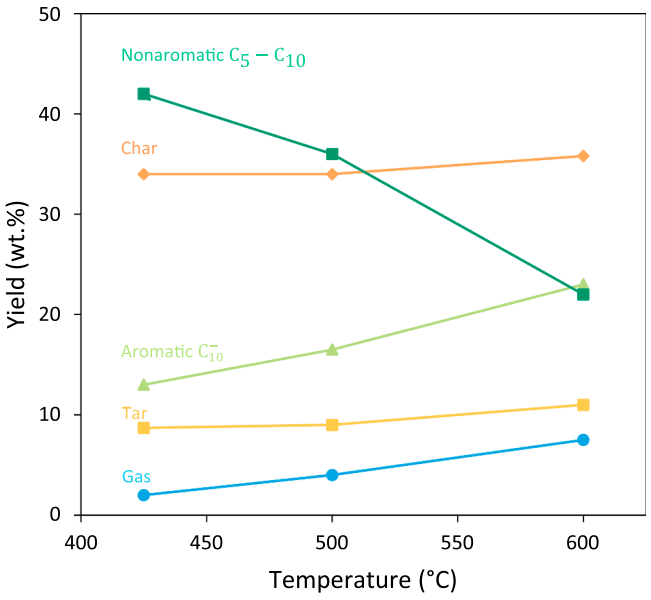


Fig. 12. Variation in product yields (tar, char, nonaromatic compounds, aromatic compounds, gas) with increasing pyrolysis temperature (425–600 °C) in a conical spouted bed reactor. Nonaromatic C_5-C_{10} content decreases with temperature due to cracking reactions; Aromatics C_{10} increases due to cyclization reaction; Gas increases due to cracking reactions. Adapted from [76].

relatively stable, indicating a lower dependence on temperature. The aromatic C_{10} fraction steadily increases, suggesting that higher pyrolysis temperatures favor the formation of aromatic compounds, which are typically found in heavier oil fractions [76]. The char yield remains stable, implying that temperature variations do not significantly influence solid residue formation. Meanwhile, the non-aromatic C_5–C_{10} fraction exhibits a marked decrease, indicating that lighter non-aromatic hydrocarbons undergo further decomposition at higher temperatures, likely contributing to gas formation or secondary reactions. Overall, higher pyrolysis temperatures induce a shift from non-aromatic liquid fractions to more stable aromatic compounds and gases, while char yield remains relatively unchanged. This trend suggests that increased thermal cracking at higher temperatures promotes the breakdown of lighter hydrocarbons into gaseous products and aromatic structures.

The ternary diagram (Fig. 13) illustrates the relative yields of char, oil, and gas from pyrolysis across various temperature ranges. Each point represents a specific dataset, with the color indicating the temperature interval (*e.g.*, 300–400 °C). Data for this analysis were collected from scientific literature published between 2015 and 2025, providing a

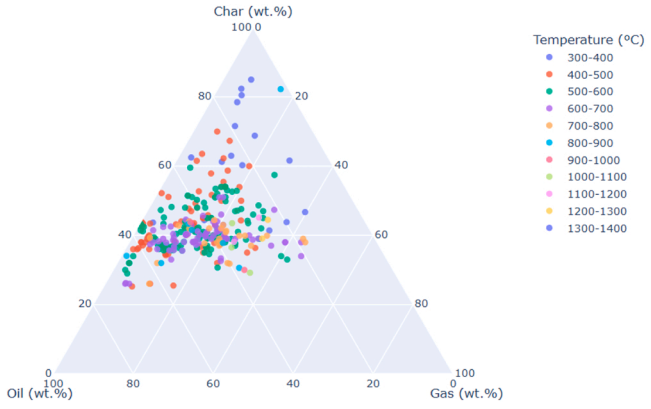


Fig. 13. Ternary diagram displaying the influence of pyrolysis temperature, in the range 300–1400 °C, on product distribution (char, oil, gas), compiled from literature published between 2015 and 2025.

comprehensive overview of experimental results from various studies.

Although the data span from 300 °C to 1400 °C, most of the data focuses on the 400–600 °C range, commonly identified in the literature as an optimal window for maximizing oil yield. In general, lower temperatures favor char formation, while higher temperatures lead to increased gas production. This behavior aligns with the well-established pyrolysis mechanism, where higher thermal energy promotes secondary cracking reactions, enhancing gas formation while reducing liquid and solid residues. At intermediate temperatures around 400–600 °C, the liquid phase becomes the major product.

2.4. Pressure

The pressure applied during the pyrolysis of ELT significantly influences product distribution, quality, and the behavior of volatiles in the reactor.

High pressure slows down volatiles' removal, increasing their residence time [39]. This prolonged exposure to higher temperatures causes the volatiles to undergo secondary cracking reactions, breaking them into smaller organic compounds [77]. As a result, higher pressures generally lead to an increase in char yield, due to the retention of volatiles within the solid phase, while gas production is favored under lower-pressure conditions, where volatiles can escape the reactor more rapidly. In contrast, reduced pressure or vacuum conditions promote rapid release of volatile matter from the surface and pores of the solid phase, reducing secondary reactions and leading to a higher yield of pyrolysis oil and gas while decreasing char formation [39]. For instance, Pantea *et al.* [78] conducted pyrolysis experiments at 490 °C, and found that under atmospheric pressure (100 kPa) the raw rCB yield was 40.5 wt%, with 55.5 wt% oil and 4.0 wt% gas, whereas under vacuum (10 kPa) the raw rCB yield was 36.5 wt%, with 55.6 wt% oil and 7.9 wt % gas. Similarly, Gao *et al.* [39] noted that increasing the pressure to 2.0 MPa, at 600 °C, resulted in a char yield increase from 32.51 wt% to 35.89 wt%, demonstrating that elevated pressure enhances char formation by suppressing volatile release.

While vacuum conditions reduce raw rCB yield, they minimize secondary cracking reactions, leading to a cleaner char with improved surface area and reduced carbonaceous residue. For example, Pantea *et al.* [78] found that the carbonaceous residue on char was significantly lower under vacuum than at atmospheric pressure, indicating a more efficient removal of unwanted organic deposits. Additionally, Roy *et al.* [79] demonstrated that combining vacuum conditions with high pyrolysis temperatures reduces hydrocarbon adsorption on the CB surface, thereby preventing the formation of carbonaceous deposits and yielding a char with improved properties, like CB used in tire manufacturing.

The impact of pressure on char quality is also evident in its physical properties. For instance, in pressurized pyrolysis, the char surface can become clogged with pyrolysis oil, reducing its pore diameter and specific surface area [39]. Char obtained under vacuum conditions has been reported to have a lower carbon deposition, which enhances its surface area and porosity, making it suitable for high-value applications [39]. Wang *et al.* [80] reported that at 600 °C, vacuum conditions resulted in a char yield of 32.51 wt%, while under a pressure of 2.0 MPa the char yield increased to 35.89 wt%. However, the specific surface area of the char decreased from 64.33 $m^2 g^{-1}$ under vacuum to 58.06 $m^2 g^{-1}$ under high pressure highlighting a trade-off where high pressure increases char yield but compromises its structural characteristics. These findings emphasize that pressure control is a critical factor in optimizing the balance between char quantity and quality for specific applications.

2.5. Particle size

The particle size of the feedstock (rubber crumb from ELT) plays a critical role in the pyrolysis process, affecting the heat transfer, reaction kinetics, and ultimately the distribution and characteristics of the resulting products [15]. Some recent studies have investigated the impact of particle size on the yield and quality of pyrolysis products [65, 81,82].

Smaller particle sizes enhance the rate of heat transfer and increase heat absorption efficiency, due to their larger surface area-to-volume ratio and lower internal limitations to mass and heat transfer [77]. As a result, finer particles promote faster degradation of the tire material, leading to higher yields of pyrolysis oil and lower yields of char [77]. Conversely, larger particle sizes tend to result in a higher char yield due to slower heat transfer and a more pronounced temperature gradient within the particles [83]. The yield of tire char has been reported to increase with particle size. Mui *et al.* [84] reported that tire char yield increased from 35.15 wt% to 37.15 wt% when the particle size increased from 500 to 710 μm to 1000–2000 μm. However, larger particles lead to lower heating rates, affecting the efficiency of pyrolysis and the overall energy consumption of the process [39]. Dai *et al.* [50] verified that larger particle sizes decrease the heating rate and favor carbonization, resulting in higher char yields and lower gas and oil yields. Larger particles are also associated with increased ash and sulfur content in the char, which can reduce its carbon content and quality [84]. Mui *et al.* [84] found that as the particle size of the feedstock increased, from 500 to 710 μm to 1000–2000 μm, ash content increased from 7.84 wt% to 8.93 wt%, sulfur content increased from 1.40 wt% to 1.67 wt%, and carbon content decreased from 88.88 wt% to 81.24 wt%. Li *et al.* [65] investigated the influence of particle size on the quality of pyrolysis products at 600 °C and found that reducing the particle size of waste tire feedstock enhances the production of high-quality pyrolytic carbon and low-sulfur pyrolysis oil. Their study revealed that larger tire particles tend to produce greater amounts of sulfoxide, sulfone sulfur, and sulfate compounds, while smaller particles promote the formation of more inorganic sulfides.

2.6. Residence time

The residence time plays a significant role in determining the yield and composition of liquid and gaseous products obtained from ELT pyrolysis. Short residence times lead to higher yields of liquid oils rich in light aromatic compounds, like limonene, as there is insufficient time for extensive cracking [20]. Conversely, longer residence times result in lower oil yields due to secondary cracking of the vapor phase, which converts heavier hydrocarbons into lighter gases [50]. Consequently, gases like hydrogen, methane, carbon monoxide, and carbon dioxide are produced in greater quantities as residence time increases, shifting the composition towards more permanent gases and lighter hydrocarbons [50]. Zhang *et al.* [66] investigated the influence of residence time on both the yield and composition of pyrolysis products. Their study demonstrated that increasing the residence time from 10 to 60 min resulted in a gradual decrease in char yield from 47.7 wt% to 39.5 wt% and a reduction in oil yield from 42.25 wt% to 37.5 wt%. In contrast, the gas yield rose significantly from 10.05 wt% to 23 wt%, supporting the conclusion that prolonged residence times enhance secondary degradation and cracking reactions. These processes promote the breakdown of condensable vapors and solid residues into lighter, non-condensable gases. Furthermore, Zhang *et al.* [66] observed that extended residence time enhanced the isomerization of limonene into alkatrienes and their subsequent aromatization into aromatic hydrocarbons.

Residence time also impacts the yield and composition of char obtained in ELT pyrolysis. Shorter residence times result in char with higher volatile content, as there is limited time for complete devolatilization [39]. As the residence time increases, the char undergoes further devolatilization, reducing its volatile matter content and improving its thermal stability and carbonization. However, excessively long residence times can also lead to a reduction in char yield due to continued thermal degradation. Mui *et al.* [84] demonstrated this effect in their study, where tire char yield decreased from 38.45 wt% to 35.66 wt% as the residence time increased from 1 to 4 h. Additionally, their findings revealed that prolonged residence times led to a reduction in carbon

content and an increase in ash and sulfur content, indicating changes in the composition and quality of the char with extended heating durations.

The ternary diagram presented in Fig. 14 illustrates the distribution of pyrolysis products – char, oil, and gas – across different residence times, ranging from less than 5–240 min. The data, compiled from scientific literature published between 2015 and 2025, provides a comprehensive overview of experimental results from various studies. Notably, most experiments were conducted with a residence time of 60 min, 30 min and 10 min. The color-coded data points, representing different durations, reveal a clear trend: shorter residence times generally favor higher oil yields, while longer residence times shift the product distribution towards increased gas production and reduced char content. This pattern is consistent with the thermal decomposition behavior of waste tires, where shorter reaction times limit secondary cracking reactions, resulting in a higher yield of condensed oil fractions, whereas extended residence times promote further breakdown of intermediates into gaseous products, thereby reducing both char and liquid yields.

Additionally, residence time is closely linked to pyrolysis temperature and the particle size of the feedstock. Higher temperatures promote cracking reactions and their rates of reaction, enabling shorter residence times, while lower temperatures require longer residence times to achieve adequate breakdown of hydrocarbons. Similarly, the size of the feedstock particles plays a significant role: larger particles need more time for complete processing, whereas smaller particles allow for shorter residence times due to their higher surface area and faster heat transfer [77]. Therefore, optimizing these three parameters –temperature, particle size, and residence time – is essential to maximize the yield and improve the composition of pyrolysis products. Moreover, in industrial applications the optimization of these parameters is particularly crucial as it directly influences the process productivity, the reactor design, and, consequently, the overall system costs.

2.7. Batch vs continuous and co-current vs counter-current process

Pyrolysis reactors can be broadly categorized into batch and continuous systems based on their mode of operation. Batch reactors are designed to process feedstock in discrete quantities. In these systems, the feedstock is loaded into the reactor, pyrolyzed, and then the reactor is emptied before the next cycle begins. This mode of operation is typically simpler to design and easier to control, making it ideal for small-scale applications or experimental setups. Batch reactors are often used in research and development, where precise control over reaction parameters is required to study the effects of temperature, residence time, or feedstock composition. However, the main limitation of batch reactors is their lower throughput, making them unsuitable for large-scale or industrial operations where continuous feedstock processing is needed.

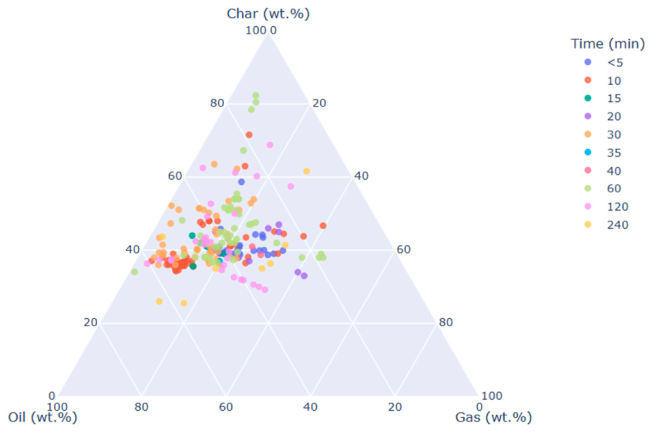


Fig. 14. Ternary plot showing how residence time affects product distribution in ELT pyrolysis, based on literature data spanning short (< 5 min) to extended (240 min) residence times.

In contrast, continuous reactors are designed for uninterrupted operation, where feedstock is continuously fed into the system and products are simultaneously removed. This design is more complex, requiring precise engineering to manage steady-state conditions and consistent heat transfer. Despite the complexity, continuous reactors are far more efficient for industrial-scale pyrolysis, as they can handle large volumes of feedstock and maintain stable operation over extended periods.

In pyrolysis, co-current and counter-current systems refer to the directional relationship between the flow of solid material and the pyrolysis vapors or gases within the continuous reactor. Pyrolysis systems can operate in co-current or counter-current configurations, referring to the directional relationship between the flow of solid material and of pyrolysis gases within the reactor. In a co-current setup, the raw rCB and pyrolysis vapors move in the same direction along the reactor, while in a counter-current configuration they flow in opposite directions. Counter-current systems tend to produce a more purified raw rCB because this configuration avoids prolonged contact between the raw rCB and vapors, at the final stages of the reactor, reducing the risk of vapor compounds depositing on the raw rCB.

2.8. Microwave pyrolysis

Various alternatives to conventional pyrolysis have been explored to improve product distribution, quality, or process efficiency. These alternatives include vacuum, pressurized, microwave, plasma, hydrogenation, co-pyrolysis, and catalytic pyrolysis [39].

Microwave-assisted pyrolysis is a thermal conversion technology that uses electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz and wavelengths between 1 and 100 cm, that are absorbed by materials and converted into heat through dielectric heating [85]. This process enables rapid, volumetric, and energy-efficient heating that is particularly beneficial for low thermal conductivity materials such as tire rubber. The inherent carbon black within tires also enhances the process by acting as a microwave susceptor, facilitating heat generation without the need for external additives. In addition to thermal effects, microwave pyrolysis may induce non-thermal phenomena due to electromagnetic field interactions, although the mechanisms remain under investigation [39].

A key advantage of microwave pyrolysis is its ability to achieve homogeneous heat distribution throughout the reactor volume, which promotes uniform thermal decomposition and minimizes hot spots. This leads to higher conversion efficiency, shorter processing times, and lower energy consumption compared to conventional pyrolysis. Additionally, microwave-assisted pyrolysis has demonstrated greater selectivity in product composition. Zhang *et al.* [86] reported oil yields containing up to 23.4 wt% limonene and gas fractions with as much as 54.5 vol% hydrogen, highlighting its potential for recovering valuable chemicals and fuel gases. Wang *et al.* [87] further compared the outputs from conventional and microwave pyrolysis and found that microwave treatment increased the concentrations of methane and hydrogen in the gas phase and significantly enhanced the content of high-value compounds – such as benzene, toluene, xylene, limonene, and naphthalene – in the pyrolysis oil.

Despite its many benefits, microwave-assisted pyrolysis remains at the laboratory scale because scaling this technology faces challenges, such as the high cost of continuous microwave power generation, reactor design complexity, and the inadequate understanding of the mechanism of microwave pyrolysis [39,85].

2.9. Co-pyrolysis

Co-pyrolysis of ELT with other residues such as plastics, biomass, and textile waste has emerged as a practical thermochemical strategy to

enhance pyrolysis efficiency and fuel quality. Numerous studies have confirmed that combining ELT with hydrogen-rich co-feedstocks results in synergistic effects, modifying the product distribution and composition [88,89].

Co-pyrolysis with various plastics wastes, including High-Density Polyethylene(HDPE), Low-Density Polyethylene (LDPE), Polypropylene (PP), Polystyrene (PS), and Polyethylene Terephthalate (PET) was studied by Alzahrani *et al.* [90] The co-pyrolysis of 1:1 tire-plastic mixtures resulted in significant interactions that affected product distribution and composition. Oil yields ranged from 56.33 wt% (tire/PET) to 73.50 wt% (tire/PP), while gas yields were highest for tire/PET (24.58 wt%) and lowest for tire/PS (7.61 wt%). Char yields varied between 15.83 wt% and 21.67 wt%. The co-pyrolysis with polyolefins like HDPE and LDPE reduced wax formation and increased the yield of aliphatic hydrocarbons, due to hydrogen donation and enhanced secondary cracking reactions. In contrast, co-pyrolysis with PS or PP promoted the formation of aromatic compounds (Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) and PAH) due to synergistic decomposition between natural rubber and the plastic matrix. Notably, co-pyrolysis with PET led to elevated CO_2 emissions and reduced light hydrocarbon yields, but it effectively decreased oxygenated compounds in the oil through oxygen release. These findings are supported by Yaghi *et al.* [88], who emphasized that co-pyrolysis of plastic waste with ELT improves the chemical profile of TPO, enhancing its content of fuel-relevant compounds such as benzene, toluene, and other light aromatics. They also reported that co-pyrolysis with PS can effectively remove sulfur from TPO, further upgrading its quality. Collectively, these results underscore the importance of feedstock selection and tire–plastic interaction mechanisms in tuning the composition of co-pyrolysis products toward cleaner and more valuable fuel outputs.

Co-pyrolysis of ELT with biomass has gained significant attention as a sustainable approach to improve the efficiency and environmental performance of thermochemical recycling. As reviewed by Yaghi *et al.* [88], biomass serves as an effective co-feedstock due to its role as a hydrogen donor and deoxygenating agent. This combination enhances the deoxygenation and aromatization of pyrolysis vapors, reducing the formation of undesirable oxygenated compounds in the oil phase and improving its heating value. Additionally, the presence of alkali metals and hydroxyl-rich functional groups in biomass promotes sulfur fixation in the char, limiting sulfur migration into the oil and gas fractions. Co-pyrolysis with various biomass types – including lignin, agricultural residues, and food waste – has demonstrated improved yields of mono-aromatic hydrocarbons and reduced emissions, supporting the production of cleaner, energy-rich fuels [91–93]. These synergistic effects highlight the viability of biomass–ELT co-pyrolysis as an integrated solution for waste valorization and renewable fuel production.

Singo *et at.* [94] studied the co-pyrolysis of ELT with biomass and plastic residues using a two-stage fixed bed reactor. The study evaluated the effects of varying feedstock ratios, temperatures, and the presence of catalyst. The results demonstrated strong synergistic effects, enhancing both the yield and quality of the resulting pyrolysis oil. Notably, co-pyrolysis of ELT with high-volatility plastics, such as LDPE, or with biomass, like palm kernel shell, led to higher oil yields and improved hydrocarbon content. Blending ELT with plastics significantly increased the formation of aliphatic and mono-aromatic hydrocarbons, while the addition of biomass promoted the deoxygenation of pyrolysis vapors, thereby reducing the oxygenate content in the final oil. These improvements were attributed to enhanced hydrogen availability from plastics and the oxygen-scavenging behavior of biomass, which together facilitated secondary cracking and reforming reactions. Overall, the findings support the viability of multi-residue co-pyrolysis as an effective method for converting complex waste streams into cleaner, energy-dense pyro-oils, contributing to sustainable waste valorization and renewable fuel generation [94].

Textile-based co-pyrolysis has also been explored. Dziok *et al.* [95] investigated the co-pyrolysis of ELT with cotton and polyester in a fixed-bed reactor at 500 °C. The addition of textiles significantly influenced product distribution: with increasing cotton content, gas yield rose from 5 wt% to 26 wt%, oil yield dropped from 62 wt% to 19 wt%, and char yield increased from 33 wt% to 43 wt%. In contrast, increasing polyester content led to gas yields rising from 3 wt% to 27 wt%, oil yields decreasing from 61 wt% to 30 wt%, and char yields decreasing from 34 wt% to 28 wt%. These changes highlight the strong impact of textile composition on pyrolysis behavior. Beyond yields, the incorporation of cotton improved char calorific value and reduced non-biogenic CO_2 emissions, while polyester enhanced adsorption capacity due to a synergistic effect [95]. However, both materials negatively affected oil quality: cotton increased water content and aqueous-organic fractions, whereas polyester produced solid oil products (oligomers) and additional solid residues, reducing the overall energy content. Gas quality also declined, with a rise in carbon oxide concentrations, though this is considered a minor concern since the gas is typically reused for process heating. Despite observed reductions in sulfur and non-biogenic CO_2 emissions, unresolved challenges – particularly the high zinc content in char and the need for oil upgrading – remain and require further development to improve overall process efficiency and fuel quality.

In conclusion, co-pyrolysis of ELT with plastics, biomass, and textiles offers a promising strategy to enhance fuel quality and waste conversion efficiency. Plastics improve hydrocarbon yields via hydrogen donation, biomass aids deoxygenation and sulfur fixation, and textiles enhance char properties.

3. Analysis of patented pyrolysis processes and products

While academic literature and patents both contribute to the advancement of pyrolysis technologies, their focus and objectives differ significantly. Scientific publications primarily aim to deepen the fundamental understanding of pyrolysis mechanisms, explore the effects of process variables, and characterize pyrolysis products under controlled experimental conditions. These studies often emphasize lab-scale experiments, data interpretation, and material analysis. Patents are driven by the need to protect novel technologies and often concentrate on applied engineering solutions, such as reactor design, process scalability, energy integration, and operational efficiency. By examining both sources, this review offers a comprehensive perspective on the current state of ELT pyrolysis – from foundational research to industrial-scale implementation – and helps identify innovation gaps and future research directions.

A comprehensive review of over 40 patents, issued between 1974 and 2022, reveals a diverse range of pyrolysis technologies developed for the thermal decomposition of waste tires and rubber-based materials. These innovations encompass various reactor configurations, process types, and operational conditions (pyrolysis temperature, residence time and operating pressure) aimed at optimizing product yield, improving process efficiency, and enhancing the quality of end-products, such as rCB, oil, and gas. A summary of the information acquired is presented in Table 4.

3.1. Temperature

The pyrolysis operating temperatures reported in these patents generally range from 200 °C to 1400 °C, with most systems optimizing conditions between 400 °C and 600 °C. For example, patent US 7,037,410 B2 [96] specifies a temperatures range of 300–650 °C, with an optimal window of 425–450 °C, for processing both granulated and whole tires. Similarly, patent EP 0 913, 360 A1 [97] describes the use of a stirred reactor operating between 400 °C and 600 °C, with a preferred range of 450 °C-550 °C. Patent US 6,736,940 B2 [98] recommends pyrolysis temperatures above 400 °C, ideally between 450 and 500 °C.

Several patents also propose multi heating stages or compartmentalized reactor designs, which help to prevent cross-contamination between process streams and allow for energy integration between stages.

Table 4
Summary of selected patents related to the pyrolysis of waste tires and rubber-derived materials. Includes key process parameters such as reactor type, temperature range, residence time, pressure conditions, and notable innovations aimed at improving product yield and quality.

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
Chamber									
US 6,244,198 B1	2001	Rubber and plastic waste, polymeric waste, slaughterhouse waste	Batch	Reactor w/ 5 sections: pre-heating, heating, pyrolysis, pre-cooling and cooling chambers	Pre-heating: 80 °C; Heating: 120–180 °C; Pre-cooling: 300 °C; Cooling: T_{amb}	-	-	Cross-contamination does not occur; Possibility to have numerous systems in parallel and energy integration between the heating and cooling stages; Pseudo-continuous system if having 1 batch per chamber.	[99]
US 7,037,410 B2	2006	Granules or compacted whole tires	Batch	2 reactors operated in tandem	300–650 °C, pref. 425–450 °C	8 h per cycle	1 atm (±10 mm Hg)	Syngas is fed to reactor 1 to cool the solid fraction and is recycled to reactor 2 to pre-heat the rubber; Pressure inside the chamber is controlled by removing gas in the same proportion as formed by rubber degradation; Feedstock loaded in trays (granules) or hung (whole tires) to ease the release of volatiles.	[96]
US 2008/ 0286192 A1	2008	Hoses, seals, miscellaneous rubber articles, tires, plastic feedstocks, medical waste, mixtures; Whole tires or fragments (pref.); 10x10'' up to 3×3''	Batch	Thermal processor (reactor) and porous container (boxes for feedstock)	T_0: T_{amb} or T_{final} of previous cycle; T_1: 288–343 °C; T_2 = 410–466 °C; T_{final} = 49–71 °C	Up to 8 h comprising: Purge: 10 min; Ramp 1: 40–60 min; t_1 @ T_1: 5–15 min; Ramp 2: 90–120 min; t_2 @ T_2: 30–60 min; Cooling	5–10 % of 1 atm	Controlled gas flow to avoid dragging significant quantity of particulate matter; Fuel and gas removed mainly in 1st heating stage; Maximum temperature set to avoid graphitization of the solid product; Presence of volatiles in the solid fraction claimed to minimizing dusting and ease the dispersion in elastomer and oil applications.	[121]
EP 2 465 904 A1	2012	Scrap tires; Granules (*E.g.* 50x50 mm)	Continuous	Furnace	350–440 °C	-	-	Process w/ sulfur transfer catalyst (3 % $CaCO_3$ and 10 wt% zeolite A−4) in a proportion of 0.3 wt% in relation to feedstock, which prevents the agglomeration of the solid material and higher activity; Inorganic load from the feedstock and catalyst is reduced in the milling	[132]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
								process, where the ashes are removed in the classifier.	
US 9,346,030 B2	2016	Rubber Granules 3–10 cm	Batch	Chamber designed as a shell and tube heat exchanger	300–400 °C	-	1–2 atm	Combustion gases used for heating are replaced by syngas when available in enough quantity; Reaction stops when pressure tends to 1 atm; Cooling of the solid fraction w/ water spray; The solid material is then mixed w/ the liquid hydrocarbons, which soaks the material and is added to a high temperature cyclone reactor where the aggregates are destroyed, and the ash and carbon are separated.	[120]
EP 4 101 909 A1	2022	Rubber mixtures, plastics, new or used tires including industrial and construction site tires, truck, passenger car and two-wheeler tires; Whole tires or shreds	Batch	Chamber	Pre-heating: 50–200 °C; Pyrolysis: 300–900 °C, pref. 500–650 °C	0.1 s−10h, pref. shorter 1 h; Advantageous embodiment for fast-pyrolysis: 0.1–20 s	Below 1 atm, pref. 0.9 atm	Lower pressures determine fast removal of volatile compounds avoiding condensation and formation of carbonaceous residues; Carbon black w/ improved properties as greater reinforcing effect in mixtures for technical rubber articles and other plastics due to surface activation w/ "reaction gas": CO, CO_2, SO, SO_2, SO_3, SO_4, NO, N_2O_3, NO_2, H_2O and O_2 or mixtures thereof.	[116]
Conveyor reactor									
US 4,030,984	1977	Scrap tires; Whole tires	Continuous	Horizontal tube reactor w/ screw conveyor	Pre-heating: 121–316 °C, pref. 177–232 °C; Pyrolysis: 316–982 °C	Pre-heating: 10 min	Pre-heating: positive pressure; Reactor: below 1 atm, pref. 2–5 in of Hg	Feeding and pre-heating in a cone shaped tire holding and melting apparatus, where melted materials are fed to the reactor and non-meltable materials (metal belts or bead materials having size above 2 in) remain on the cone base.	[134]
US 4,062,304	1977	Polymeric and/or inorganic waste, vulcanized rubber, old tires, Shreds	Continuous	Tube reactor with auger	-	Controlled by the reactor angle	Below 1 atm	By varying the angle of the blades, the speed of pre-heating/pyrolysis/ discharge zones can be adjusted; The reactor vessel	[112]

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Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
								can be tilted to ensure complete pyrolysis of liquids or paste-like materials.	
US 4,084,521	1978	Rubber and plastic wastes; Granules 30–50 mm	Continuous	Rotatable shaft or worm conveyor reactor	400–800 °C	Controlled by the conveyor speed	Below 1 atm, w/ a gradient of 30–40 mm H_2O in the direction of the movement	Pressure gradient ensures that solids and gases flow together in one direction and cannot flow back; Hot air flows inside the shaft in opposite direction of the solid material to improve the heat transfer.	[115]
US 4,648,328	1987	Tire Shreds3x3'' or less	Continuous	Reactor w/ chain and flight conveyor	Pre-heating: 149–316 °C; Pyrolysis: 427–871 °C, pref. 510–621 °C (max oil, less syngas); Final temperature: 538–649 °C	20–60 min	-	Multiple pyrolysis stages (4 zones), where temperature increases in each zone (independent heating); All parts that contact the pyrolysis gases are coated with aluminum and/or aluminum oxide; Conveyor flights scraping the interior of the reactor to prevent buildup of solid material which would interfere with the feeding; The advantage of continuous heating is to avoid exposure to initial high temperature which would lead to a rapid evolution of gaseous and liquid hydrocarbons from the interior of the shreds, causing the fragments to "explode".	[105]
US 4,839,151	1989	Used vulcanized articles, more specifically used tires; Whole tires	Continuous	Pre-heating and Pyrolysis 1: chamber w/ flat-bed conveyor; Pyrolysis 2: chamber w/ ceramic paddles	Pre-heating: (27−49)-(149−232) °C; Pyrolysis 1: (93−260)-(427−538) °C; Pyrolysis 2: 816–982 °C	-	Pre-heating: 5–20 psig; Pyrolysis 1: −5–20 psig	Combustion gases from pyrolysis used to produce steam for the pre-heating; Particulate matter dragged w/ vapor stream collected in cyclone system at high temperature; Removal of fines in the vapor stream by the condensation of the heavier hydrocarbons; Particulate matter are joined w/ the solid stream to further processing (pyrolysis 2).	[103]
US 6,758,150 B2	2004	Solids and/or mixtures w/ liquid/ sludge; Rubber, herbicides, pesticides, plastics, wood, paper, etc. Granules	Batch or continuous	Screw conveyor w/ 2 independent retorts	1st stage: 649–982 °C; 2nd stage: residual heat from the material	-	Below 1 atm	Continuous feeding by rotary airlock: small compartments prevent blockage during the feeding;	[113]

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Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
					+ good isolation			Pyrolysis in the second retort achieved w/ heat retained by the material, no additional heat is added; Modular and compacted pyrolysis system.	
US 6,835,861 B2; US 7,341,646 B2	20042008	Hydrocarbon materials, rubber, coal, tar sands, etc. Shreds	Continuous or batch	Continuous: reaction chamber w/ a helicoid auger; Batch: reaction chamber and batch apparatus	Batch: T_1: 60–454 °C, pref. 68–288 °C; T_2: 288–454 °C; T_3: T_2 Continuous: 232–454 °C, pref. 288 °C	-	Below 1 atm, pref. 5–10 in Hg	Low energy method to release carbon black from tires rather than being created during the pyrolysis; Process divided in 3 stages - 1st phase (activation): energy supply until oil condensation initiates, 2nd phase (decomposition): exothermic reaction (no energy is added), 3rd phase (completion): decomposition reaction slows down, temperature starts to decrease and energy is provided; The addition of catalyst leads to a 25 % reduction of the fuel consumption, reaction time and temperature, and eases the vapors release.	[135]
US 6,736,940 B2US 7,329,329 B2	20042008	Steel belted radials, car, truck and other motor vehicle tires; Whole tires or shreds (pref.); Below 2 in300–1100 kg/h, pref. 900–1000 kg/h	Continuous or batch (pref. continuous)	Reactor w/ a pin auger screw	Above 400 °C pref. 450–500 °C	Controlled by the auger speed	Below 1 atm, pref. −60–125 Pa	Vapors and solid flow through the reactor in countercurrent; Expansion tank at the end of the reactor allows separation of vapors and solids, being the gas stream in contact w/ paddles that minimize the amount of solids that are dragged; Vapor stream is fed to a separator and contacts w/ an oil spray that removes particulate matter from the gas stream and promotes condensation of heavy oils and tars (prevent fouling) that can be reintroduced in the pyrolysis reactor.	[109]
US 7,416,641 B2	2008	Automobile tires; Granules pref. 2 in	Continuous	Rotary screw conveyor with appendages	Variation of 0.1 % allowed	Controlled by the screw speed	-	The screw conveyor controls the residence time,	[110]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
				(spikes, paddles, blades or similar) arranged in a broken helix pattern				promotes desorption of volatiles by agitating the material bed and prevents hot spots; Particulate matter in the vapor stream reduced by controlled agitation and reduced velocity of the pyrolysis gas inside the reactor; This process avoids temperature gradients by feeding only when the temperature reaches the set point; Solid product is pulverized immediately to ensure uniform size, break fiberglass strands, allow faster cooling and break free contaminants (*e.g.*. SiO_2 and ferrous particles); Oil purification system comprising filtering particulate matter and removing PAH.	
US 2011/ 0107668 A1	2011	Waste tires, plastics, wood, agricultural biowaste; Shreds(*e.g.*, 3–7 cm)	Continuous	Reactor w/ auger blades	Pyrolysis: 350–550 °C, pref. 350–450 °C; Reformer: 250–400 °C, pref. 250–350 °C	Pyrolysis: 40–70 min; Reformer: 30–60 min	-	Solid product reformer reduces the content of impurities such as organic volatiles in the material; Gas barrier prevents gas products of the pyrolysis from entering the reformer; Volatile stream in co-current w/ the solids; Part of the resulting oil is introduced into the 1st condensation stage to remove particulate matter.	[107]
US 8,425,731 B2	2013	Rubber products, new or used tires; Granules; 10 mm	Continuous	Reactor w/ rotating drag chain conveyor	500–800 °C	-	Below 1 atm	Collection of 5 by-products: steel, oil, syngas, flue gas and carbon black.	[136]
US 2013/ 0064754 A1	2013	Rubber waste, in particular scrap tires; Granules	Continuous	Reactor w/ screw conveyor comprising worms w/ pitches	1st stage: 100–200 °C, pref. 150–180 °C; 2nd stage: 200–300 °C; 3rd stage: 300–600 °C, pref. 400–550 °C; Purification: ≤ 800 °C	Pyrolysis: 2–4 h each stage; Purification: 2 h	20–50 mbar	The process comprises 3 heating zones - 1st stage: depolymerization of rubber w/ emission of light oils, 2nd stage - emission of medium heavy oils, 3rd stage: pyrolysis w/ emissions of heavy oils; Slow thermal	[100]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
								treatment to avoid formation of carbonaceous residues.	
US 8,354,070 B2	2013	Waste tires; Chips	Continuous	Reactor w/ moving chain w/ disks	-	-	-	The reactor is composed by 2 tubes on top of each other: the material is fed to the 1st tube, is moved along the tube by a chain having a plurality of disks, falls into the 2nd tube and is driven through its length until the discharge; The vapor stream flows in the same direction as the solid in 1st tube and exits from the top of the reactor; The conveying system prevents accumulation inside the tubes, avoiding coking phenomenon.	[137]
US 2016/ 0083657 A1 (Thermolysis)	2016	Waste materials; Shreds	-	Reactor w/ worm screw conveyor	200–700 °C, pref. 400–600 °C	Controlled by the speed of the auger	Max. 5 bar	Process w/ water as a chemical reagent.	[119]
US 9,663,662 B1 (Thermolysis)	2017	Scrap tires; Shreds	Continuous	Reactor w/ one or more helical screw conveyors	T_1: 300–700 °C; T_2: 700–890 °C; T_3: 700–890 or > 900 °C; T_4: 80–300 °C	-	1 atm	Multiple screw conveyors allow different speeds in distinct zones of the reactor; The addition of water as a chemical reagent makes it possible to control quality characteristics of the materials, namely production of high porosity carbon black; Higher quantities of water and higher temperatures may contribute to products close to ASTM CB N100 and N200, while reduced temperatures and steam concentration produces materials closer to ASTM CB N600 and N700.	[122]
EP 3 627 050 B1	2018	Waste tires; Shreds (large or small)	Continuous	Reactor w/ double flight screws	-	-	-	Stacked screws allow reducing the equipment expansion and the load on the screws by reducing its length; Feedstock is vaporized along the first screw (90 %) and second screw (10 %); Combination of vapors outlet	[138]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
								above the feedstock feeding screw: capture of lighter fuels.	
US 10,428,277 B2 (Thermolysis)	2019	Rubber scrap; Chips	Continuous	Reactor w/ twin-screw conveyor	Feedstock: 30–40 °C; Steam: 700–800 °C; Reactor: 500–600 °C; Cyclone: 350–400 °C	Controlled by the speed of the auger	Above 1 atm	Process w/ water as a chemical reagent; Screws rotate towards each other, increasing the mixing of the feedstock and increasing heat transfer; Plates installed along the full length of each screw to slide on the surface of the heating pipes and remove any solid soot that is formed.	[118]
US 10,731,081 B2	2020	Polymer waste solid or liquid	Continuous	Reactor w/ screw auger w/ different configurations	T_1: T_{amb}; T_2: T_{amb}−104 °C; T_3: 104–300 °C; T_4: 300–366 °C; T_5: 366–488 °C; T_6: 455–982 °C; T_7 < 982 °C	t_1 < 1 min; t_2 < 3 min; t_3: 15–45 min; t_4: 30–120 min; t_5: 30–90 min; t_6: 15–60 min; t_7: 15–30 min	P_1: 1 atm; P_2: 0.9–1 atm; P_3: in-situ P; P_4: in-situ P; P_5 < 5.0 psig; P_6 < 0.8 psig; P_7 < 1 psig	Different configurations of the screw auger allow progressive temperature zones to achieve optimal temperature ramps, control residence time in each zone and achieve optimum product mixing; Pyrolysis gases, nitrogen and/or steam can be injected into the reactor to increase the vapor stream, reducing residence time and over-cracking of the molecules.	[102]
Rotary kiln									
US 3,823,221	1974	Vulcanized scrap rubber	Batch or continuous	Bartlett-Snow calciner	538–1371 °C, pref. 649–982 °C	-	-	Patent focused on upgrading methods: steam activation and acid washing to achieve reinforcing agents.	[131]
US 5,225,044	1993	Tires, plastic waste, coal, garbage, asphalt, oil shale	Continuous	Rotary drum	650 °C	Defined and adjusted by the angle of the pyrolysis reactor	Above 1 atm (*e.g.,* 5 psig)	Volatiles removed near the feeding end; The reactor includes a scrapper to remove material that is adhered onto the inner walls.	[126]
US 5,853,687	1998	Rubber waste; Granules2–5 mm	Batch or continuous	Rotating furnace	600–1100 °C	15–200 min, pref. 25–75 min	1 atm	Quality of the product is independent of the composition of the initial load and comparable to commercial carbon black.	[111]
US 5,728,361	1998	Waste materials; Whole tires or granules (pref.) Less than 5×5 cm	Continuous	Rotary kiln	T_1 > 275 °C, pref. 385 °C; T_2: 400–650 °C,pref. 520–540 °C	Above 20 min, pref. 20–40 min	1 atm	Volatiles removed from the reactor at both ends, reducing its residence time; Part of the syngas is recycled to the reactor to promote hydrogenation, reduce cyclization and reduce residence time.	[106]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
EP 1 163 092 B1US 6,221,329 B1	2000 2001	Scrap tires; Shreds Max. 4 in	Continuous	Rotary kiln	T_1: 700–800 °C, pref. 700–750 °C; T_2: 600–700 °C, pref. 600 °C; T_3: 500–600 °C, pref. 500 °C	Determined by the speed rotation of both the rotary kiln and the feed cylinder	-	Rotary kiln divided into a plurality of independent heating zones w/ decreasing temperature, which allows the production of commercial end products due to a more efficient pyrolysis.	[123]
US 7,497,929 B2	2009	Scrap tires; Shreds< 50 mm; 4–5 ton	Batch	Rotating retort	T_1: T_{amb}; T_2: 350 °C; T_3: 450 °C; T_4: 540 °C	Total: 3–4 h; t_1: 1 h; t_2: 1.9–2.0 h; t_3: 0.55–0.6 h	-	Possibility for surface modification treatments for the solid product.	[139]
US 8,349,285 B2	2013	Scrap rubber and scrap tires; Granules less than 2 in, pref. 1.5 in	Continuous	Rotary calciner	4 zones: 500, 550, 550, 550 °C	At least 30 min in each zone	Below 1 atm	Reaction chamber having a temperature profile comprising 4 different zones; Production of materials of high-quality levels, being its morphology and characteristics controlled by varying the pyrolysis temperature and reaction time.	[101]
WO 2013/095145 A1	2013	Scrap rubber, in particular tires w/ varying silica content (preferably less than 5 %); Granules	Continuous	Rotary kiln	1st stage: 500–800 °C, pref. 630–670 °C; 2nd stage: 550–800 °C, pref. 680–720 °C (80 °C higher than the temp. of the 1st stage)	20–50 min, pref. 30–40 min in each stage	-	Rotary kiln enables volatiles to be removed more easily; In the 1st stage, an intermediate char is produced (volatiles 5–10 wt %, pref. less than 2 wt%); In the 2nd stage (polishing stage), the volatiles are reduced to less than 1.0–2.0 wt%; Operation preferably in counter-current flow so the volatiles are drawn from the solid, not being re-adsorbed; The temperatures are set to have the condensable volatiles removed without increase the composition of the intermediate char (1st stage) and to remove the less volatile fraction without further unwanted decomposition of the char (2nd stage).	[124]
WO 2016/112371	2016	Whole tires, partial tires, pieces of tires, municipal waste, plastics and biomass; Shreds (pref.) 0.5–10 t/h, pref. 4.5–5.5 t/h	Continuous	Rotary kiln	1st stage: 316–538 °C, pref. 399–482 °C; 2nd stage: 316–538 °C, pref. 399–482 °C (Activated carbon: 760–980 °C)	30 min−5h, pref. 45 min−1.25h in each stage	1st stage: below 1 atm	Possibility to produce carbon black and activated carbon by varying the temperature of the 2nd reactor; The temperature of the 2nd reactor	[125]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
								ensures that the carbon black produced by the 1st reactor is not modified and additional carbon black is produced from unreacted hydrocarbons.	
WO 2021/158109 A1	2021	Rubber waste: tires, technical rubber goods, unvulcanized rubber slabs, strips, extrusions; Granules	Batch	Reactor 1: Furnace; Reactor 2: Rotary kiln	T_1: 350–500 °C pref. 350–400 °C; T_2: 550–850 °C pref. 700–750 °C	t_1: 8–50 h, pref. 15–40 h; t_2: 10–50 min, pref. 20–25 min	P_2 < 2000 Pa, pref. < 500 Pa	Pre-sorting of the feedstock according to their chemical compositions and to the desired rCB composition, namely low crystalline silica content.	[108]
US 2022/0251392 A1	2022	Tires; Shreds0.25–10.16 cm	Batch	Rotary kiln	1st stage: 250–350 °C; 2nd stage: above 450 °C	t_1: 1–4 h; t_2: 2–4 h; Max. 12 h	10–200 mbar	In the 1st stage, water, light hydrocarbons and part of the heaviest hydrocarbons are gasified, while in the 2nd stage, the gasification of heavy hydrocarbons is achieved; The vapor stream is sent to a flash distillation vessel, where a fraction is condensed, being the liquid heavy hydrocarbons returned to the reactor.	[117]
Stirred reactor									
US 3,978,199	1976	Vulcanized waste rubber, scrapped automotive vehicle tires; Shreds 6 in, pref. 0.25–2 in	Batch	Stirred reactor w/ an aromatic solvent oil	260–371 °C, pref. 288–343 °C	0.5–2 h	25–100 psig	A fraction of the heavy oil collected after condensation of the vapor stream is used as solvent for the pyrolysis process.	[140]
EP 0 913 360 A1	1997	Waste tires; Shreds less than 5 cm	Intermittent continuous	Reactor w/ agitator	400–600 °C, pref. 450–550 °C	30–50 min	1.0–2.5 kg/cm^2	The material is fed to the reactor and falls down in a dispersed way, and by the up and down movement of the agitator, the material appears to float, which results in an improved heat transfer.	[97]
US 6,046,370	2000	Rubber and plastics; Shreds2x2 in or less	Batch	Reactor w/ mechanical mixing	350–450 °C	-	0.5–0.9 bar	Between batches a fraction of the solid product is mixed w/ the feedstock to prevent sticking to available surfaces during the softening stage; The solid product also enhances the heat transfer and contributes to reduce the reaction time, acting as a thermal buffer and minimizing temperature variations.	[127]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
US 2009/0120335 A1	2009	Plastic, rubber materials, tires; Shreds	Continuous	Stirred reactor	Reactor 1: 200–400 °C; Reactor 2: 400–800 °C	-	1 atm	From reactor 1 to reactor 2, a screw conveyor leads to mechanical shear and impaction, grinds the material, and enhances heat transfer in the 2nd stage; Lower temperature in reactor 1 produces hydrocarbons with lower sulfur content, that are treated in separate to the hydrocarbons from reactor 2.	[128]
US 2021/0301145 (Dissolution process)	2021	Plastic or tires (light and heavy tires); Granules (<5 mm); Shreds (<20 mm)	Continuous	Stirred reactor w/ an aromatic solvent	< 425 °C, pref. 375–425 °C; In the case of 2 reactors: (i) 200–300 °C, pref. 250–280 °C; (ii) < 425 °C, pref. 375–425 °C	(i) 30 min−2h; (ii) 30 min−2h, pref. 45–90 min	< 1.5 MPa	Advantages of the liquid process: lower temperature, limits the polycondensation reactions of aromatics, lower formation of coke at the surface of the solid, lower amount of gases, particles without agglomeration; 2 reactors in series: 1st reactor - cracking of bonds between polymers (*e.g.,* S-S), 2nd reactor - thermal degradation occurs; The solvent is obtained after fractionation and is composed of pref. 80 wt% of monoaromatics (in relation to the total aromatic compounds), which makes it possible to efficiently dissolve the feedstock.	[129]
Vertical reactor									
WO 2010/127664 A1	2010	-	Continuous	Vertical reactor	300–1200 °C	-	-	Possibility to use catalyst; Pre-heating stage where the used tire granules are in contact w/ pyrolysis oil from the condensation stages, depolymerizing the surface which becomes sticky, so a powdered catalyst is mixed and attaches to the surface for subsequent cracking process (affecting the product formation).	[133]

(*continued on next page*)

Table 4 (*continued*)

Patent	Year	Feedstock	Process type	Reactor	Temperature	Residence time	Pressure	Innovation	Ref
US 9,404,042 B2	2016	Scrap tires, vulcanization residues, waste plastics; Granules	Continuous	Vertical reactor	500–600 °C	-	Below 1 atm	Vertical reactor allows homogeneous mixing and heating due to the alternately arranged heating plates; The vapor stream is extracted in the center of the reactor and transverse to the flow of solids (crossflow).	[114]
US 9,777,159 B2	2017	Tires, plastics, wood, rubber materials; Shreds	Batch or continuous (pref.)	Vertical rotary tray reactor	441–527 °C	-	1 atm (±3 in H_2O)	A thermal gradient can be used to overcome the poor heat transfer of the feedstock; Solids and vapors move in counter-current flows, allowing the capture of sulfur in the solid fraction; The solid material is collected at the bottom of the reactor, while the gas stream is removed from the top; Reduced amount of particulate matter is entrained in the vapors since gentle rolling allows aggregation and agglomeration of the carbon black particles.	[130]
EP 4 050 085 A1	2022	Plastics, vehicle tires and technical rubber items; Particles 0.1–5 mm, pref. 0.1–1 mm; 0.5–5 kg/h, pref. 0.5–1.5 kg	Continuous	Vertical reactor	450–900 °C, pref. 650–800 °C	0.1–20 s, pref. 1–10 s	-	Fast pyrolysis prevents the accumulation of hydrocarbons on the surface of the particles and their subsequent coking; Pyrolysis is completed quickly and cost-effectively; The carbon black obtained has a more active surface area which enables improved reinforcement; The solid product can be re-fed to the reactor to decrease the organic contamination.	[104]
Other configurations									
US 6,149,881	2000	Scrap tire carcasses or polyisoprene rubber; Batch: 10 g	Batch or continuous	Cylindrical open coil oven	T_1: 250 °C; T_2: 425 °C	5 min @ T_2	Below 1 atm	The coil not only supports the feedstock but also heats the material without being required an external furnace; Method optimized to produce limonene.	[141]
WO 2013/184074 A1	2013	Waste tires; Powder100 μm−25 mm, pref. 400–600 μm		Plasma thermal processor	Induction thermal processor: 900–1200 °C; Powder injector: 6000–11000 °C	-	-	Plasma process to produce carbon black and syngas.	[142]

For example, patent US 6,244,198 B1 [99] outlines a reactor with five thermally segregated zones: pre-heating, heating, pyrolysis, pre-cooling, and cooling. Patent US 2013/0064754 A1 [100] describes a screw-conveyor reactor divided into four zones, including a first stage at 100–200 °C, a second stage at 200–300 °C, a third stage at 300–600 °C, and a final purification zone operating at temperatures up to 800 °C. In a similar approach, patent US 8,349,285 B2 [101] details a reaction chamber featuring a temperature profile divided into four distinct zones, designed specifically to produce high-quality pyrolysis products. Additionally, patent US 10,731,081 B2 [102] utilizes a single screw auger reactor with configurable progressive temperature zones, allowing for precise temperature ramping, controlled residence times, and optimal product mixing.

In addition to thermal zoning, some patents incorporate energy recovery and recycling strategies to enhance process efficiency. For instance, patent US 4,839,151 [103] proposes using combustion gases from the pyrolysis process to generate steam for the pre-heating stage, reducing external energy input. Likewise, patent US 7,037,410 B2 [96] describes a system with two reactors operating in tandem, where syngas is first fed into reactor 1 to cool the solid fraction and then recycled into reactor 2 to pre-heat the rubber feedstock, demonstrating a closed-loop approach to energy utilization.

3.2. Residence time

Residence time in pyrolysis reactors varies widely, reflecting the diversity of process designs–ranging from rapid pyrolysis lasting just seconds to long-duration processes extending to several hours. Fast pyrolysis systems, such as the one described in patent EP 4 050 085 A1 [104], operate within 0.1–20 s aiming to minimize hydrocarbon accumulation on the surface of the particles and their subsequent coke formation. However, due to the short exposure it may be necessary to recycle the solid product to reduce residual organic contamination.

Intermediate residence times are common in continuous and staged systems. For instance, patent US 4,648,328 [105] employs a 20–60 min residence time in a multi-zone reactor. Similarly, patent US 5,728,361 [106] uses a rotary kiln with a residence time of 20–40 min, and patent EP 0, 913, 360 A1 [97] reports 30–50 min in a stirred reactor. Patent US 2011/0107668 A1 [107] combines 40–70 min of pyrolysis with an additional 30–60 min in a reforming stage to reduce impurities, such as residual volatiles in the solid product. On the other hand, long residence times, extending to several hours, are used in more complex or staged processes. For example, patent WO 2021/158109 A1 [108] applies 8–50 h in a primary furnace stage, followed by 10–50 min in a rotary kiln. Likewise, patent US 2013/0064754 A1 [100] reports 2–4 h in each of three pyrolysis stages and an additional 2 h in a purification stage.

Some patents, such as US 6,736,940 B2 [98], US 7,329,329 B2 [109], and US 7,416,641 B2 [110], do not explicitly state residence times. Instead, they describe systems where residence time is controlled mechanically, either by adjusting the auger or screw speed. These designs allow for dynamic residence time control tailored to the feedstock and process requirements.

3.3. Pressure

Pressure conditions described across the reviewed patents typically range from sub-atmospheric to slightly above atmospheric levels, depending on the design and intended outcomes of the pyrolysis process. Many systems aim to maintain near-atmospheric pressure, for simplicity and operational stability. For example, patent US 7,037,410 B2 [96] maintains the pressure around 1 atm by removing gas at a rate matching its formation from rubber degradation. Similarly, patents US 5,853,687 [111] and US 5,728,361 [106] operate under atmospheric pressure conditions. However, a significant number of patents (such as US 4,062, 304 [112], US 6,758,150 B2 [113], and US 9,404,042 B2 [114]) favor sub-atmospheric operation to enhance volatile removal and reduce secondary reactions. Patent US 4,084,521 [115] also operates under these pressure conditions and utilizes a pressure gradient system to direct solid and gas flows in a single direction, preventing backflow and improving separation efficiency. Patent EP 4 101 909 A1 [116] specifies operation below 1 atm, ideally around 0.9 atm, to enable rapid volatile extraction, minimizing condensation and carbonaceous residue formation. More extreme conditions are employed in patent US 2022/0251392 A1 [117], which uses a rotary kiln reactor operating between 10 and 200 mbar, and patent US 2013/0064754 A1 [100], which applies 20–50 mbar in a screw conveyor reactor. On the other end of the spectrum, patents US 10,428,277 B2 [118] and US 2016/0083657 A1 [119] describe thermolysis processes conducted above atmospheric pressure.

3.4. Reactor designs

Significant technological innovations highlighted include advanced reactor designs and integrated systems, aiming to prevent cross-contamination, increase energy efficiency, enhance heat transfer, and improve products quality. Continuous processes have become increasingly prevalent in modern patents, particularly those employing rotary kilns and screw conveyor reactors. These systems allow for greater throughput, continuous product recovery, and more consistent control of reaction parameters.

Chamber reactors used in pyrolysis have undergone notable technological advancements, with a focus on controlled reaction environments, thermal integration, and enhanced product quality. Patent US 6,244,198 B1 [99] introduces an innovative batch reactor system comprising five distinct chambers–pre-heating, heating, pyrolysis, pre-cooling, and cooling–strategically arranged to promote efficient heat recovery between the heating and cooling zones. This configuration prevents cross-contamination of pyrolysis products, enables the parallel operation of multiple chambers, and allows for a pseudo-continuous operation by managing sequential batches across different stages. Similarly, patent US 9,346,030 B2 [120] presents a chamber reactor configured as a shell-and-tube heat exchanger, which utilizes syngas, if available, as the heat source instead of combustion gases. This approach improves energy efficiency while also contributing to lower emissions. In another example, patent US 2008/0286192 A1 [121] proposes a staged heating system with precisely controlled gas flow, designed to minimize particulate entrainment and prevent graphitization of the solid residue. This enhances the quality of the resulting rCB, making it more suitable for advanced material applications.

Conveyor-based pyrolysis systems are among the most frequently described technologies in patents, reflecting their versatility, scalability, and strong control over process variables. These systems typically employ one or more screw conveyors, which allow for precise regulation of feedstock residence time and reactor temperature by adjusting the screw speed [118,122]. Beyond conveying material, the screw mechanism also agitates the feedstock promoting the desorption of volatiles, improving heat transfer, ensuring uniform thermal exposure, and preventing hot spots [110]. In configurations where screws rotate in opposite directions mixing efficiency is further improved, resulting in more consistent thermal decomposition [118].

A variety of design enhancements have been patented to optimize reactor performance and product quality. For instance, patent US 10,428,277 B2 [118] features scraper plates installed along the screw shaft, which slide along the surfaces of internal heating pipes to remove soot and residue, thus maintaining heat transfer efficiency and avoiding fouling. Similarly, patent US 7,416,641 B2 [110] incorporates paddles, spikes, and a broken helix screw configuration to prevent agglomeration, to promote better mixing, and to improve the control of gas velocities–ultimately reducing particulate entrainment in the vapor stream. In addition, US 4,648,328 [105] includes conveyor flights that scrape the reactor interior, preventing solid buildup.

Further advancements focus on multi-zone reactor designs, allowing

temperature and reaction conditions to be carefully staged throughout the process. Patent US 4,648,328 [105] describes a multi-zone conveyor system that incrementally increases temperature along the reactor length, preventing abrupt gas evolution and enhancing product integrity. Likewise, US 6,221,329 B1 [123] and US 8,349,285 B2 [101] implement four-zone thermal profiles that enable more efficient pyrolysis and the production of high-quality end products, by varying temperature and residence time to tailor the morphology and properties of the resulting materials. In US 10,731,081 B2 [102], the screw auger design allows for progressive temperature ramps, improved feedstock mixing, and precise control over residence time in each zone. Patent US 9,663,662 B1[122] explores the use of multiple screw conveyors with independent speed control, allowing different zones of the reactor to operate under distinct thermal and residence time conditions.

Additional innovations in reactor architecture include pin auger screw systems, as described in US 6,736,940 B2 [98] and US 7,329,329 B2 [109], designed for processing shredded tires with enhanced vapor-solid separation. These systems use counter-current flow of solids and vapors, with an expansion tank at the reactor outlet for phase separation. Inside the reactor, internal paddles help reduce solid entrainment in the vapor stream, while an oil spray filtration system captures fine particles, condenses heavy tars, and prevents fouling. Condensed products can then be recirculated into the reactor for further processing.

Several other patents introduce specific innovations targeting residence time and gas management. For example, US 5,728,361 [106] removes volatiles from both ends of the reactor to reduce vapor residence time, while US 10,731,081 B2 [102] describes injecting pyrolysis gases, nitrogen, or steam, to accelerate vapor flow and minimize over-cracking of hydrocarbons. Lastly, patent US 4,839,151 [103] addresses particulate control by applying controlled pressure conditions, which assist in removing fines and enhancing the purity of vapor-phase products.

Rotary kilns remain a dominant and well-established technology for continuous pyrolysis, offering robust handling of diverse feedstocks, including whole tires, shredded rubber, and rubber granules. Over the years, several innovations have been introduced in rotary kilns to optimize pyrolysis efficiency, enhance product quality, and improve operational control. Many patents describe multi-stage designs to support temperature zoning and staged thermal decomposition. For example, patents US 6,221,329 B1 [123], US 5,728,361 [106], and US 8,349,285 B2 [101] incorporate multiple heating zones with controlled temperature profiles, enabling the sequential breakdown of the rubber matrix and improving the quality of the resulting char. Further innovation is demonstrated in patent WO 2013/095145 A1 [124], which outlines a two-stage rotary kiln process. In this system, the first stage produces an intermediate char with low volatile content, while the second refining stage reduces residual volatiles further, resulting in high-quality rCB with minimal decomposition. Additionally, patent WO 2016/112371 [125] introduces a flexible two-stage rotary kiln system capable of producing either standard rCB or activated rCB by adjusting the temperature conditions, offering greater versatility and product customization.

Effective volatile removal is another focus in rotary kiln innovations. Patent US 5,225,044 [126] describes removal of volatiles near the end of the reactor feeding zone, while in US 5,728,361 [106] volatiles are extracted from both ends of the reactor – in both cases, volatiles removal reduces residence time and minimizes secondary reactions. Patent WO 2013/095145 A1 [124] employs a counter-current vapor flow to promote efficient volatile extraction and thus helps to prevent re-adsorption, a common issue in less optimized systems. Moreover, US 5,225,044 [126] integrates a scraper mechanism to remove materials adhering to the inner reactor walls, thereby maintaining heat transfer efficiency and reducing operational downtime.

Stirred reactor technologies have introduced some innovations by enhancing heat and mass transfer and improving reaction uniformity. Patent EP 0 913 360 A1 [97] describes a reactor equipped with an agitator employing vertical up-and-down movements, which causes the feedstock to disperse and float, significantly improving heat distribution and ensuring uniform pyrolysis. Similarly, patent US 6,046,370 [127] utilizes mechanical mixing to blend solid residues from previous batches with fresh feedstock. This approach prevents sticking during the softening stage and leverages previously pyrolyzed materials as a thermal buffer, stabilizing temperatures and shortening process duration.

Further advancements include multi-stage stirred reactors designed for more controlled and targeted pyrolysis. Patent US 2009/0120335 A1 [128] introduces a two-stage system with distinct temperature zones, enabling the selective production of low-sulfur hydrocarbons. In this patent, an intermediate screw conveyor provides mechanical shear, improving feedstock grinding and enhancing heat transfer in the second stage. Patent US 2021/0301145 A1 [129] describes a different approach based on liquid-phase pyrolysis using aromatic solvents, allowing for lower operational temperatures and suppressing polycondensation and coke formation. This solvent-assisted method enhances feedstock dissolution and promotes cleaner, more efficient thermal degradation, yielding purer pyrolysis products.

Vertical reactor designs have introduced several innovations to improve feedstock mixing, product quality, and heat transfer efficiency in pyrolysis processes. Patent US 9,404,042 B2 [114] describes a vertical reactor equipped with alternating heating plates, which ensure uniform thermal distribution and facilitate effective mixing of the feedstock. This configuration also enables the central and transverse extraction of vapor streams, significantly enhancing vapor-solid separation efficiency. In a similar approach, patent US 9,777,159 B2 [130] presents a vertical rotary tray reactor that utilizes a controlled thermal gradient to address the poor heat transfer characteristics of polymeric feedstocks. This reactor promotes a gentle counter-current flow of solids and vapors – solids move downward and are collected at the bottom, while vapors exit from the top. The soft rolling motion of materials encourages aggregation and agglomeration of rCB particles, thereby reducing the entrainment of particulates in the vapor phase and improving the purity of the recovered gases and oils.

3.5. Other innovations

Recent advancements in pyrolysis technologies increasingly focus on producing high value rCB with enhanced surface properties and reduced impurity content, aligning with industrial quality standards. For instance, patent EP 4 101 909 A1 [116] utilizes gases, such as CO, CO_2, SO_x, NO_x, H_2O, and O_2, either individually or in combination, to promote surface activation of rCB during pyrolysis. Similarly, patent US 3,823,221 [131] employs a Bartlett-Snow calciner and focuses on post-treatment methods, like steam activation and acid washing, to upgrade rCB into a material suitable for use as a reinforcing agent.

A notable innovation is the use of thermolysis processes with water as a reactive medium, explored in patents US 2016/0083657 A1 [119], US 9,663,662 B1 [122], and US 10,428,277 B2 [118]. In these systems, water not only aids in decomposition but also modifies rCB porosity and surface characteristics, enabling tailoring of the final product properties to meet specific ASTM standards. For example, patent US 9,663,662 B1 [122] notes that higher water content and elevated temperatures yield rCB with characteristics like N100 and N200 CB grades, which are known for their high surface area and reinforcing potential. In contrast, lower temperatures and reduced steam levels produce rCB with properties closer to N600 and N700 CB grades, which exhibit lower surface activity. These thermolysis processes often utilize screw-conveyor reactors, allowing for precise control of residence time and temperature, and, in some designs, enhanced mixing and heat transfer through opposing screw rotation.

Additionally, the integration of catalysts and additives is being explored to further improve pyrolysis efficiency and product quality. Patent EP 2 465 904 A1 [132], for instance, introduces sulfur transfer catalysts such as $CaCO_3$ and zeolite 4A, which help prevent

agglomeration of solid products and promote higher catalytic activity. In patent WO 2010/127664 A1 [133], a vertical reactor design introduces a powdered catalyst that attaches to the rCB surface and thus facilitates in-situ cracking reactions, influencing both product distribution and quality.

Overall, the reviewed patents collectively illustrate advancements towards more controlled, efficient, and environmentally sustainable pyrolysis processes, leveraging innovative reactor designs, precise process control, catalytic enhancements, and energy-efficient practices. A summary of the reviewed patents and gathered information is presented in Table 4.

4. Conclusions and future directions

Pyrolysis of ELT is increasingly recognized as a viable and sustainable pathway for waste valorization, enabling the recovery of valuable products such as energy-rich gases (syngas), tire pyrolysis oil (TPO), and solid carbonaceous materials (raw rCB).

This review has examined the current technological landscape, including reactor configurations, operating conditions, product characteristics, and recent industrial innovations. Each of the principal reactor types (fixed bed, fluidized bed, auger, rotary kiln, and stirred) presents specific design trade-offs depending on the intended product distribution, the characteristics of the feedstock, and the desired processing scale.

The influence of key process parameters such as temperature, pressure, particle size, and residence time is well established. TPO yields are generally maximized within the 500–600 °C temperature range, while higher temperatures tend to favor gas formation and improve the structural quality of the resulting char. Operating under reduced pressure enhances the removal of volatiles and contributes to the production of cleaner raw rCB. At the same time, smaller particle sizes and shorter residence times typically lead to higher oil recovery. Although these trends are observed consistently across reactor designs, their full optimization at industrial scale remains an ongoing challenge.

Among the outputs of pyrolysis, raw rCB holds considerable promise, particularly in the context of circular tire manufacturing. Nevertheless, its widespread application is currently constrained by variability in surface area, ash content, morphology, and the presence of adsorbed volatiles. Similar issues affect TPO, which, despite its energy content and chemical potential, requires upgrading to meet the performance and regulatory standards necessary for commercial use.

Although technological advancements have been considerable, especially with the development of fluidized and auger reactors that offer enhanced scalability compared to fixed-bed systems, industrial implementation remains relatively limited. Main technical barriers include the need for continuous operation, effective heat integration, and control over secondary vapor-phase reactions. Innovations such as multi-zone heating and twin-screw reactor configurations show promise in addressing these challenges, yet there is still a lack of long-term data from commercial-scale facilities.

In addition to technical development, a more comprehensive assessment of end-of-life tires pyrolysis is needed. Life cycle assessments and techno-economic analyses are underutilized but essential for evaluating environmental performance and financial feasibility. The adoption of digital tools (such as real-time monitoring, artificial intelligence, and process simulation) could enhance system efficiency, flexibility, and decision-making, especially under variable operational conditions.

To enable broader deployment of pyrolysis technology, future research must focus on developing modular and scalable reactor systems with integrated energy and product recovery capabilities. It is equally important to improve the quality and standardization of rCB through advanced post-treatment and certification methods. In parallel, upgrading strategies for TPO and expanded valorization of syngas should be pursued to enhance overall economic viability. Strengthening life cycle assessments and techno-economic analyses will help benchmark sustainability, inform policy, and de-risk investment. Moreover, the integration of digital process control technologies offers a pathway to operational optimization. Finally, supportive regulatory frameworks and industrial partnerships will be vital to foster market uptake and build robust circular value chains between tire manufacturers, recyclers, and end-users of recovered materials.

As circular economy principles gain traction globally, ELT pyrolysis offers a valuable bridge between waste management, resource recovery, and industrial decarbonization. Continued innovation, supported by policy, investment, and collaboration across sectors, will be key to unlocking its full potential in the coming decades.

CRediT authorship contribution statement

Silva Carlos: Writing – review & editing, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Inês Portugal:** Writing – review & editing, Supervision, Formal analysis, Conceptualization. **Adélio Mendes:** Writing – review & editing, Resources, Funding acquisition, Formal analysis. **João Rocha:** Writing – review & editing, Validation, Supervision, Formal analysis. **Costa Sebastião:** Visualization, Methodology, Investigation, Data curation. **Cristiana Maganinho:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Silva Clara:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis, Data curation.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT (OpenAI) in order to assist with writing and improving the clarity of the text. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.118667.

Data availability

Data will be made available on request.

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