

Tire pyrolysis char: Processes, properties, upgrading and applications

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ABSTRACT

Waste tires are solid wastes with large annual output and with the potential for great harm to the environment. The pyrolysis of waste tires can recycle energy and produce reusable products. Although there are many reviews in the literature in regard to the pyrolysis characteristics of waste tires, no one paper focuses on reviewing and summarizing the tire char. This paper critically appraises the achievements of earlier reports and literature and assesses the current state-of-the-art for the production and application of tire char from waste tires. Initially, the thermal decomposition behavior of different tire rubbers is discussed and compared where it is shown that the different components of waste tire rubber have different thermal degradation characteristics. The influencing factors on the yield and quality of tire char are discussed and assessed in terms of different pyrolysis reactors and technologies, tire type and composition, and a range of pyrolysis process conditions. The composition of the waste tire and pyrolysis conditions are the main factors affecting the distribution of pyrolysis products. Pyrolysis technology and reactor equipment also have an effect on the distribution of pyrolysis products. The physical and chemical structural characteristics of tire char are critically reviewed in detail, including a comparison of the fundamental differences with commercial carbon black and modified tire char (physical activation and chemical activation). Finally, high-value application fields and developmental prospects of tire char are summarized. Through extensive literature review, a novel development was that tire char could be used as a source of graphene. The economic analysis of the various tire char applications should be one of the main research directions in the future. The keynote of this review is to promote intensification of waste tire recycling and treatment so that more tire char can be obtained from waste tire pyrolysis and thereby be reused in different applications to obtain more value.

1. Introduction

The rapid development of the automobile and transportation industries has led to a sharp increase in the annual output of waste tires [1–4]. It is estimated that more than 3 billion tires are produced each year with an expectation of continuing market demand growth of over 4% [5]. Inevitably, there will also be billions of end-of-life waste tires produced, requiring waste management, treatment, and disposal [6]. Stockpiling and improper disposal of waste tires causes problems to the environment through providing sites for vermin or breeding grounds for insects and the potential of fire hazard of large tire dumps (Fig. 1).

Material recovery options for waste tires include recycling as rubber [7,8] and rubber particles [9,10] for use as rubber flooring for sports fields and playgrounds and their use as civil engineering application materials [11]. The treatment and disposal methods applied to waste tires in some countries also includes disposal in waste landfill [12,13]. However, waste tires do not readily degrade in landfills because of the presence of strong cross-linking of sulfur bonds and rubber in the tire rubber formulation [14,15]. Therefore, there is a recent impetus to find more sustainable and higher value resource-recovery options for the treatment of waste tires.

Pyrolysis is a promising method of recycling, and energy and fuels

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Fig. 1. The harm of waste tires on the environment.

recovery in the field of waste tire treatment, which could meet the three principles of solid waste treatment: reduction, resource recovery, and mitigation of pollutants. Compared with other treatment methods (i.e. combustion [16,17], retread, and landfill [18,19]), using pyrolysis as a recovery method has been widely researched since it results in reduced secondary pollution of the environment and the potential for the higher economic value of products. The pyrolysis process degrades the organic components of waste tires to obtain gases, condensable oil [20], and solid char [21,22]. Accordingly, the transformation of waste tires to alternative fuels allows for reduced use of conventional fossil fuels, therefore, waste tire pyrolysis has been demonstrated to be a feasible way to indirectly reduce greenhouse gas emissions [23]. In addition, the steel reinforcement of the tire can be recovered from the residual char for recycling back into the iron and steel industry [22,25].

Pyrolysis technology has developed and matured enough over time to be regarded as a rapid and efficient treatment option to solve the environmental problems caused by waste tires. The steel, rubber, carbon black, additives, and other materials contained in the waste tire may be recovered and almost no waste by-products are produced from the pyrolysis process [24]. Fig. 2 illustrates the products and by-products from waste tire pyrolysis. With proper processing and modification, for example through pyrolysis oil and gas treatment, reforming of product volatiles [25], chemical impregnation modification of char [26], char activation by steam [27] or CO₂ [28], the pyrolysis products could be used as fuel gas or fuel oil [29,30], a rubber reinforcement agent [31, 32], pollutant adsorbent [33], high-value chemicals [34,35], and other resource materials [36].

The main product obtained from tire pyrolysis under mild conditions is pyrolysis oil, however, its direct utilization as a fuel oil is conditioned by high sulfur content and composition [37,38]. In this respect, the

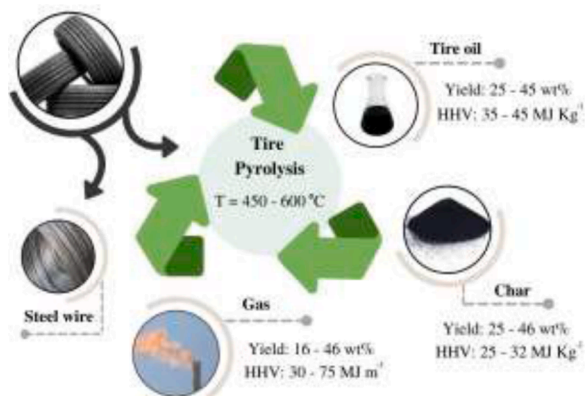


Fig. 2. The pyrolysis products of waste tires.

development of catalytic pyrolysis has been explored to increase the selection of high-value chemicals such as benzene, toluene, and xylenes (BTX). However, it is worthy of note that different supported noble metals such as Ni, Co, Pd and Pt showed different catalytic performances [39,40]. Thus, improving the quality of pyrolysis products is the main challenge for the full-scale development of the waste tire pyrolysis process. It has been reported that several industrial-scale tire pyrolysis projects have not reached full commercial success due to the limited value of the obtained products [41].

A bibliometric analysis reveals the increasing attention to waste tire valorization by pyrolysis in recent literature with more than 1700 papers published since the year 2000. The search term “tire pyrolysis” in the search fields of, “title, abstract, and keywords” were performed using the Scopus database. Fig. 3 shows the evolution of the number of published papers dealing with tire pyrolysis and the number of citations received by these papers in the Scopus database. As observed, since 2000, the number of papers published per year has increased by 8 times. Along the same line, the increase of the impact of this topic in scientific literature is even more remarkable, currently reaching more than 6000 citations year⁻¹. The total number of citations is more than 38,000 with a high index of 90, which evidences the great interest of this tire valorization route in the scientific community.

China has the highest contribution to the tire pyrolysis literature followed by Spain, the United States, India, and United Kingdom. Fig. 4a shows the distribution of the most active countries in tire pyrolysis research. Tire pyrolysis studies were mainly published in Chemical Engineering and Energy and Fuels journals. The leading journal in this field is the Journal of Analytical and Applied Pyrolysis with more than 110 papers (6.5% of the total number of published papers), followed by Fuel (5.1%), Waste Management (3.3%), Energy and Fuels (2.5%) and Fuel Processing Technology (2.1%). A detailed distribution of the leading journals publishing tire pyrolysis research articles is shown in Fig. 4b.

The most active research group in this field is that headed by Prof. Martin Olazar from the University of the Basque Country. Other groups with significant contributions to tire pyrolysis research are those led by Prof. Christian Roy (Université Laval), Prof. Paul Williams (Leeds University), and Prof. Ramón Murillo (Instituto de Carboquímica Zaragoza).

Early literature has reported a great deal of information about the various applications of waste tires and there are several reviews on waste tire pyrolysis. For example, a detailed review on recycling waste tire rubber and associated environmental considerations have been presented [42]. The overviews of the properties and utilization of waste tire rubber in concrete were also reported [43,44]. It was also reported that the recycling methods of waste tires, the influence of pyrolysis conditions on tire pyrolysis products, and the application of the

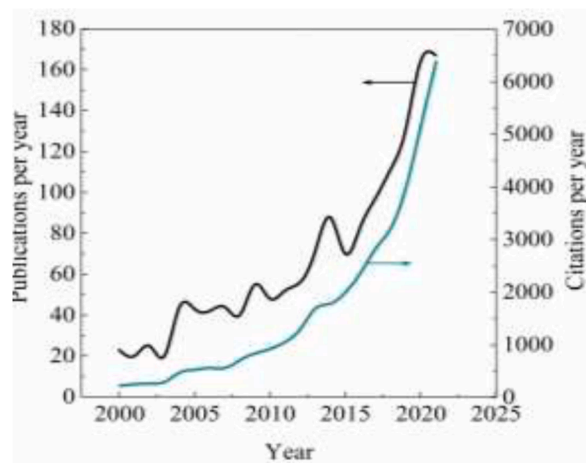


Fig. 3. Evolution of the paper number of tire pyrolysis published and their impact in the 2000 to 2021 period.

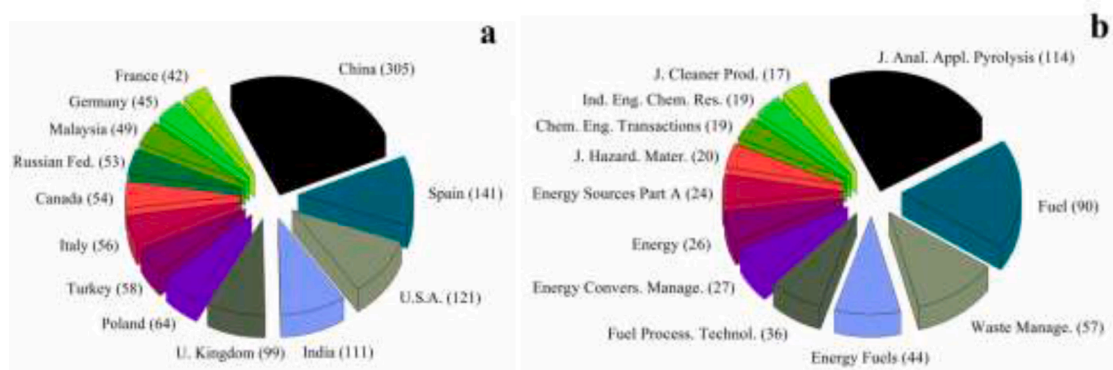


Fig. 4. Top countries in tire pyrolysis research (more than 40 contributions), 4a, and leading indexed scientific journals (more than 15 publications) (4b).

pyrolysis products (oil, gas, and char) [45]. The influence of different reactor types on the efficiency and proportions of waste tire pyrolysis products has been discussed [46]. Though the waste tire pyrolysis technology and product applications were summarized [21], the applications of tire char were not comprehensively covered. Arabiourrutia et al. [47] analyzed the latest advances in waste tire valorization using catalytic pyrolysis with a special focus on catalysts, reaction mechanisms, and product properties. Although various authors have reviewed waste tire treatment in terms of waste tire recycling methods, pyrolysis technology, and pyrolysis products application, none of their work included an in-depth review of tire pyrolysis char and did not include suggestions for further research areas on the topic.

Tire char is one of the main pyrolysis products obtained from waste tires, whose economic value is a vital factor to determine the continued development of the commercialization of waste tire pyrolysis [48]. Many studies have reported on improving the quality and application of tire char. Based on these previous studies, this paper provides a comprehensive and critical review of waste tire derived char and aims to promote the development of this technology from the following aspects: (1) the waste tire pyrolysis principle; (2) the main factors affecting the properties of tire char; (3) the physical and chemical characteristics of tire char; (4) the modification and high-value applications of tire char; (5) the developments and future trends in the research and development of tire char. In particular, this paper discusses the thermo-gravimetric analysis of different waste tire rubbers; a comprehensive comparison of influencing factors (pyrolysis reactor, pyrolysis technology, pyrolysis conditions, tire type, and composition) on the yield and quality of tire char; the physical/chemical characteristics of tire char and commercial carbon black are discussed and compared; a discussion on the advantages and disadvantages of different modification methods of tire char; reviewing the use of tire char as adsorbents, catalysts and supporting materials, reinforcing agent and storage materials.

2. Properties of waste tire

2.1. Tire type and composition

According to the various requirements and working environment of tires (long-distance, load, and pressure) and environmental requirements (road quality, temperature, humidity), the compositions of tires can be very different. Waste tires can be simply classified as light vehicle tires (LVT), medium vehicle tires (MVT), and heavy vehicle tires (HVT). A large proportion of natural rubber (NR) exists in LVT (bicycle tires), the highest proportion of styrene-butadiene rubber (SBR) is found in MVT (car tires) and a high proportion of butadiene rubber (BR) is present in HVT (truck tires) [49]. The exact composition of tires depends on brand [50] and type [51]. In MVT (car tires) and HVT (truck tires), the amount of carbon black present could reach 28 wt. %, which is much higher than that of only 11 wt. % in LVT (bicycle tires) [52]. Many

attempts using various analytical methods (Thermal Gravimetric-Fourier Transform Infrared Spectrometry (TG-FTIR) [53–55], Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC/MS) [56,57], Thermogravimetric-Differential Scanning Calorimetry (TG-DSC) [58], Thermogravimetric-Mass Spectrometry (TG-MS), etc.) have been implemented in the field of the determination of the composition of waste tire rubber. Danon et al. [59] have determined and identified the rubber composition of waste tires using de-volatilization kinetics. Tire rubber mainly includes mixtures of NR, BR, synthetic rubber (SR), and SBR. Other tire composition results have also been reported by other researchers [55,57,60,61].

In addition to the different types of rubber, a typical tire also contains carbon black, metals, textiles, and additives (silica, vulcanization agents). The main influence of carbon black is to improve the abrasion resistance of the tire, moreover, it is a cheap anti-ozonant and also contributes to extracting heat from the tread and belt to avoid thermal damage to the tire. The role of steel is to provide support and strength to tires. Sulfur as a vulcanizing agent increases the elasticity of tires and improves their strength and hardness [62], and zinc oxide acts as an activator to accelerate the vulcanization of rubber with sulfur [63]. However, the quantities of these components in the tire formulation are different depending on the requirements of tire manufacture and properties. Table 1 shows the basic components of eight different types of tires.

Usually, the major part of the tire is rubber (about 45–47 wt. %) [4] due to its good elasticity and shock absorbance properties. Because of the low production and high price of natural rubber, the rubber used in tires is a mixture of NR (polyisoprene) and SR (e.g. SBR) in different ratios depending upon the specific use. These rubbers are mainly used in the sidewalls (22 wt. %) and the treads (32.5 wt. %) [4]. If carbon black and silica (comprising about 21–22.5 wt. %) are not added to the tire composition, the mechanical and wear resistance of the tire will be very poor [4].

The carbon black structure aids the constant elongation stress and modulus of the rubber and tire rubbers require a suitable composition of carbon blacks of different particle sizes to attain the desired performance. The smaller the particle size of the carbon black, the better the reinforcing performance and wear resistance. Reinforced carbon black with fine particle size is mainly used in the tire tread, endowing tires with excellent wear resistance. The higher the carbon black structure, the higher the constant elongation stress and modulus and the better the distribution within the rubber. The rubber compound needs a suitable composition of carbon blacks of different particle sizes. In the other parts of the tire, the rubber material is required to be resistant to flexural cracking, ozone oxidation, with good elasticity and low thermal performance. To achieve these objectives, a coarse particle size of semi-reinforced carbon black (specific surface area less than $40 \text{ m}^2 \cdot \text{g}^{-1}$) is generally chosen. The third vital components in tires are metal reinforcement, which is included at more than 12 wt. %. The ratio of metal

Table 1

The composition of tire depending on the required use.

Material	Car tire	Truck tire	Off-road tire	Passenger tire	Truck tire	LVT	MVT	HVT	Comments
Rubber/Elastomers (wt.%)	47	45	47	47	45	48% NR 10% SR	14% NR 27% SR	27% NR 14% SR	Different synthetic and natural rubber are used, e.g. natural rubber (polyisoprene), chloroprene rubber, butadiene rubber, polybutadiene rubber, synthetic rubber, etc.
Carbon black and silica (wt.%)	22.5	21	22	21.5	22	11	28	28	To strengthen the rubber and aid abrasion resistance
Metals (wt.%)	14	23.5	12	16.5	21.5	14-18	14-25	14-25	Steel belts and cord for strength
Textiles (wt.%)	5.5	1	10	5.5	-	-	-	-	Used for reinforcement
Vulcanization agents (wt.%)	2.5	3	3	-	-	-	-	-	Used to facilitate production process
Additives (wt.%)	8.5	6.5	6	7.5	5	12-16	16-17	16-17	additives used to partial replacement carbon black (such clay)
Sulfur (wt.%)				1	1	1.4	1.88	2.09	Used to cross link the polymer chains within the rubber, harden and prevent excessive deformation at elevated temperatures
Zinc oxide (wt.%)				1	2	-	-	-	As an activator to accelerate the vulcanization of rubber with sulfur
Refs.	[4]	[4]	[4]	[22]	[22]	[52]	[52]	[52]	

in truck tires reaches 23.5 wt. %, whereas, the metal ratio in off-road tires and car tires is between 12 and 14 wt. % [4]. The content of vulcanization agents in tires is minimal, at between 2.5 and 3.0 wt. % [4]. Vulcanization agents play an important role in the durability of tires. Additives are compounds that improve processing properties such as pressure sensitivity and hot melt of the rubber [64] and are added at between 6 and 8.5 wt. % [4]. The yield of additives in car tires could reach 8.5 wt. %, but in off-road tires are typically 6 wt. %. Vulcanization accelerator is one particular additive, which is good at promoting shortening the vulcanization time and decreasing the vulcanization temperature of rubber. Vulcanization accelerators used in tires also could reduce the use of vulcanization agents (sulfur) and increase the mechanical properties of the rubber. The most common accelerator is ZnO which also acts as a vulcanization activator. According to the different compositions of tires, the nature and source of tire char will also be different. The carbon in tire char is derived both from the pyrolysis of rubber and also from the carbon black and additives [65].

2.2. Thermal properties

Pyrolysis is a technology for energy and resource recovery from many different types of wastes at the appropriate temperature and is carried out under inert conditions. The thermal decomposition characteristics of wastes investigated with thermo-gravimetric (TG) analysis determine the mass change of samples concerning temperature or time [66]. Moreover, the relevance of this technique lies in the capacity to

also obtain a preliminary rubber composition and to determine pyrolysis kinetics [67]. To analyze the TG curves, the higher the DTG value, the faster the degradation reaction and consequently the easier the sample is decomposed. Heating rates of between 1 and 100 °C·min⁻¹ have been used for the evaluation of tire pyrolysis kinetics in the reported literature [68], however, intermediate values are the most suitable. On the one hand, the use of too high heating values provokes severe heat transfer limitation to the sample and a displacement of the DTG curve to higher temperatures. On the other hand, low heating rates greatly lengthen the duration of the experiment.

The TG curves of waste tires are generally similar, but some differences exist due to the diversity of the rubber formulation and composition of additives used in tire manufacture [49,69]. Danon et al. [70] studied the thermal decomposition behavior of waste bicycle tires. According to the TG and DTG curves, waste tire thermal decomposition consisted of two stages involving tire rubber decomposition and decomposition of pyrolysis products derived from secondary pyrolysis [71] (as shown in Fig. 5a). The first stage involves the decomposition of the different components of the tire which decompose at different temperatures; (i) The plasticizers and other additives in tires start to decompose at 150-200 °C and there is a little yield of oil/gas produced [62,72]. At temperatures higher than 250 °C, pyrolysis oil and gas are produced; (ii) Between 250 and 500 °C, NR [73] and SBR/BR [74] are degraded [75]. Between 450 and 500 °C, the maximum release of liquid products takes place then a further increase provokes a decrease [76]. At temperatures higher than 550 °C, volatiles is degraded completely, and

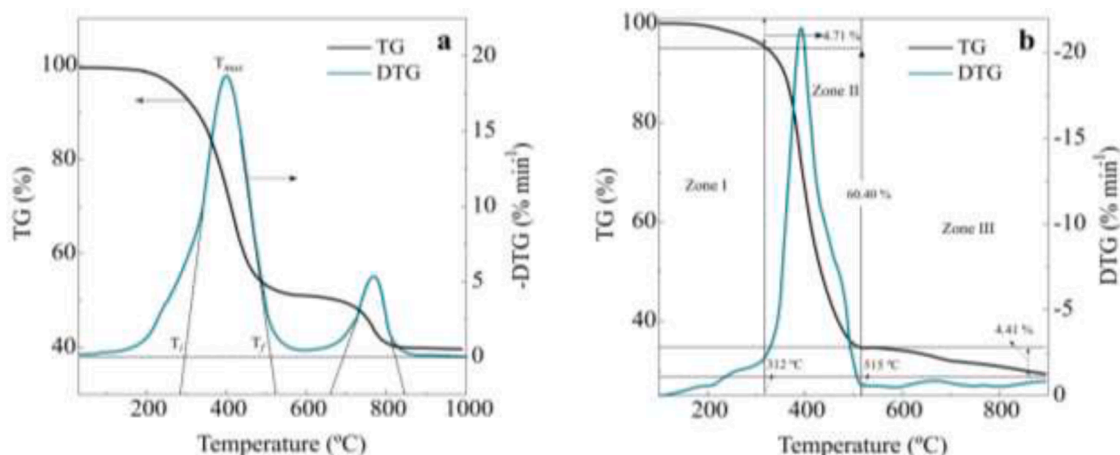


Fig. 5. TG/DTG curves for waste bicycle tire at 50 °C·min⁻¹ heating rate (a) [71] and waste car tire at 30 °C·min⁻¹ heating rate (b) [79].

tire rubber is almost completely decomposed [77]. The second stage involves secondary cracking of the produced pyrolysis products that mainly takes place in the temperature range of 660–850 °C, which has also been reported in the works of Han et al. [78] and Li et al. [76].

Some researchers have suggested that tire decomposition can be divided into three zones [66]. In the first zone, nearly 5 wt. % mass loss occurs due to the decomposition of the light volatiles existing in the waste tire (Fig. 5b) [79]. The second zone is the main decomposition zone which takes place between temperatures of 300 and 500 °C with about 60 wt. % mass loss, which occurs since the main components (rubbers) of the waste tire start to decompose within this temperature range [59]. The third decomposition zone refers to the secondary cracking of pyrolysis products, which takes place in the temperature range of 600–900 °C. These results show good agreement with other literature [5,80]. The TG thermogram in Fig. 5 shows that the residual product of tire pyrolysis is more than 33.0 wt. % of the initial weight, and consists of fixed carbon and ash [81,82].

The typical TG and DTG thermograms of tire decomposition shown in Fig. 5a and 5b show that the components of waste tires exhibit different and complicated thermal degradation behavior. The division of the waste tire rubber pyrolysis stages completely depends on the different interpretations of the individual researchers. Although researchers have divided the thermal degradation behavior of waste tires into two or three stage segments according to mass loss and weight loss rate, the last stage is always attributed to the generation of the secondary reactions of the pyrolysis product. Three-stage degradation behavior is a more detailed description and analysis of the two-stage degradation behavior. More detailed division of the stages of thermal degradation of waste tires can be: 0–100 °C, moisture volatilization; 100–320 °C, decomposition of the volatiles in the waste tire, which is shown both in Fig. 5a and 5b; 320–530 °C, NR degradation; 450–550 °C, SBR/BR degradation (these two stages are shown in Fig. 5b); 500–600 °C, the volatiles in rubber are completely pyrolyzed; > 600 °C, the pyrolysis products are cracked into small molecular products. Although this division is more detailed, it also has some defects since it is not clear how the composition of the tire rubber, e.g. NR and SBR/BR exist in the waste tire rubber. Reports on TGA of tires commonly show two peaks of tire rubber degradation, which suggest that NR and SBR are present in most tire rubber studied in the literature, but detailed rubber composition is rarely presented [83,84]. It is also not clear what the pyrolysis products are in the secondary cracking zone reported in the literature.

At present, most research based on thermo-gravimetric analysis has been used to establish an accurate dynamic model and calculate the mass loss of waste tires with time and temperature change. There are a range of kinetic models developed for the decomposition of waste tires. The use of TGA for the pyrolysis of the tire and the different kinetic approaches proposed was reported in the literature [68]. A single-step decomposition model for waste tire rubber was once proposed [85]. However, it was a simplified model and did not provide a reasonable explanation for the different mass loss peaks observed in the pyrolysis thermogram curve because the reaction rate of the different reaction steps was not suitably predicted. Therefore, the use of the single-step decomposition model has not been popular. Aylón et al. [86] built a model based on the DTG thermogram of the waste tire. They calculated the pyrolysis activation energy of the main components of the tire and reported that the activation energy of the additives in the waste tire was 70 KJ mol⁻¹, the activation energy of SBR was reported as 212 KJ·mol⁻¹, and the activation energy of NR was 265 KJ·mol⁻¹. Iso-conversion or model free methods have been widely applied in TGA studies for the assessment of kinetic parameters (activation energy) without considering an explicit model. In this approach, TGA results under varying heating rates for the same conversion value are considered for the determination of activation energy for each conversion point [87]. Friedman, Kissinger, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose methods are the most commonly applied methods in this category [88]. Thus, the pyrolysis of truck and passenger

tires using Friedman and Kissinger methods was analyzed [89], moreover, the performance of both methods was compared and the reaction mechanism was discussed. Alsarakji et al. [90] applied the iso-conversional method proposed by Ozawa-Flynn-Wall for the evaluation of thermal and catalytic pyrolysis of waste tires using NiO and MgO catalysts. Thus, the obtained kinetic parameters were of specific interest for the evaluation of the kinetic role played by each catalyst. A wide study comparing several kinetic approaches has been carried out [91], including iso-conversional methods and other conventional kinetic approaches. A significant increase in the activation energy in relation to truck and car tire pyrolysis was determined using the Friedman method by Chen et al. [92]. Thus, the low activation energies for conversion values below 0.2 correspond to the dehydration and decomposition of processing oils, whereas the higher activation energies for higher conversions are associated with the decomposition of NR and/or SBR. Recently, a quasi-isothermal TGA approach for the evaluation of the tire pyrolysis reaction mechanism was proposed [57]. This procedure evidenced eight decomposition zones associated with different reactions taking place during waste tire pyrolysis.

In the pyrolysis of waste tires, the kinetic data is different due to the different pyrolysis conditions. Under the same pyrolysis conditions, different brands and models of tires have different components and contents (such as the different ratios of SBR, BR, black carbon, and other additives), resulting in the different internal structures of tire rubber. With the different tire rubber structures, the rate of heat transfer, and heat absorption varies greatly, resulting in different changes in the process of rubber molecular cracking and thermal weight loss. Therefore, there is no general trend that can explain the changes in the composition of waste tires.

Because the source and the composition of the waste tire were different in different literature reports, the TG/DTG thermograms consequently varied. Although none of the research papers reports a comprehensive TG/DTG analysis for the waste tire, each provides data for the waste tire pyrolysis industry.

3. Influencing factors on the yield and quality of tire char

The quality and yield of tire char strongly depend on the original tire composition and pyrolysis process conditions and also play a significant role in terms of the economic feasibility of the waste tire pyrolysis process [21,93,94]. To improve the quality of tire char, it is necessary to understand the influencing factors and how they relate to the quality of tire char. Several factors affect the quality of tire char in different ways, and the influencing mechanisms are also different. The quality and yield of tire char are determined by the following factors: (i) type of pyrolysis reactor (fixed bed, fluidized bed, conical spouted bed, and rotary kiln reactor) [46]; (ii) type of pyrolysis process (vacuum pyrolysis, microwave pyrolysis, hydrogenation pyrolysis, co-pyrolysis, and catalytic pyrolysis) [95]; (iii) operating conditions [45] (temperature, pressure, residence time, carrier gas (N₂, CO₂), particle size, catalyst); (iv) other factors such as original tire composition. In general, fast pyrolysis conditions ensure quick tire particle heating and rubber degradation. Therefore, the violent release of pyrolysis volatiles inside tire particles promotes their fast diffusion towards the outside. These conditions minimize secondary condensation reactions of pyrolysis volatiles and reduce solid product formation. Thus, the char yield obtained in fast pyrolysis is usually slightly higher than the carbon black content of original tire rubber, i.e. in the 25 to 35% range. However, the opposite effect can be observed under slow pyrolysis conditions with a higher extent of secondary reactions, higher char yields, and carbon black adulteration. In this latter case, the char yield usually ranges between 35 and 45%. Moreover, the original tire composition also plays a significant role in char yield and characteristics. Thus, depending on tire brand and application (light or heavy vehicle, motorcycles etc.) variable contents and compositions of rubber and carbon black are used. In this respect, different authors have studied the pyrolysis of different tire materials

under the same experimental conditions and reported significant differences in char yields and their main features, for example the char surface area [50,96].

3.1. Pyrolysis reactor

The pyrolysis process is performed in an inert gas atmosphere (e.g. N_2 [97], Ar [98], He [99], pyrolysis gas [100]). The use of carrier gas ensures the operation is maintained under inert conditions and avoids the presence of air in the reaction environment and the subsequent oxidation of the organic material in the pyrolysis process. The flow velocity of the inert gas could influence the reaction environment, residence time, and pyrolysis product yield and composition. The inert gas flow velocity and the size and specific gravity of waste tire particles determine the particle behavior in the pyrolysis reactor. The different structures of pyrolysis reactors affect the yield and quality of pyrolysis products of the waste tire. According to the classification of two-phase (gas-solid) flow models given in the literature, pyrolysis reactors have different dispersion coefficients (D , $m^2 \cdot s^{-1}$) and gas flow velocity (v , $m \cdot s^{-1}$) [101]. According to the dispersion coefficient and gas flow velocity, the following models are defined: fixed bed ($D = 0.0-0.02 m^2 \cdot s^{-1}$, $v = 0.02-0.6 m \cdot s^{-1}$) [102,103], fluidized bed ($D = 0.001-0.6 m^2 \cdot s^{-1}$, $v = 0.015-0.7 m \cdot s^{-1}$) [104–106], conical spouted bed ($D = 5 \times 10^{-4}-0.06 m^2 \cdot s^{-1}$, $v = 0.1-0.5 m \cdot s^{-1}$) [107,108], rotary kiln reactor ($D = 0.0-0.35 m^2 \cdot s^{-1}$, $v = 0-0.7 m \cdot s^{-1}$) [109–111]. It is worthy of note that dispersion coefficients evaluate the degree of back-mixing and quantify the deviation from ideal plug flow behavior. Therefore, this coefficient is of great interest to the design and operation of chemical reactors, since it determines the residence time distribution in the reactor. This parameter is

of especial relevance in tire pyrolysis due to its role in the extent of secondary reactions and the distribution of pyrolysis products. Moreover, the heating rate is another parameter affecting pyrolysis performance that was considered in the reactors classification. Thus, fixed beds are usually operated under slow heating rates in the $5-40 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ ranges [73,83,112–114], the effective heating rate attained in rotary kilns depends on several factors such as the reactor size, rotation speed, or the use of heat carriers (as steel balls). Finally, both fluidized bed and spouted bed reactors guarantee fast heating of tire particles and reach effective heat values with high heating rates of $10^3-10^4 \text{ }^\circ\text{C} \cdot \text{s}^{-1}$ [115, 116].

3.1.1. Fixed bed

At present, the fixed bed reactor is one of the main types of waste tire pyrolysis equipment used in laboratory-scale studies due to its ease of operation [117,118] and low cost [119]. However, these reactors are mainly operated in the batch mode, i.e., the tire material located in the reactor is slowly heated while the formed pyrolysis volatiles are continuously purged from the reactor using an inert gas stream. Accordingly, the obtained results are regarded as preliminary and prior to a continuous demonstration or commercial scale operation. Fixed bed reactors can be divided into vertical fixed bed [112] (Fig. 6a), horizontal fixed bed [120] (Fig. 6b), one-step catalytic fixed bed [121] (Fig. 6c), and two-step catalytic fixed bed [24] (Fig. 6d). The main advantages of a fixed bed for the pyrolysis of waste tires are: (i) the back-mixing is small [122,123], liquid and catalyst can be removed effectively; (ii) the mechanical loss of catalysts is small [124]; (iii) the structure of the fixed bed is simple [125]; (iv) the fixed bed is suitable for dealing with any size and shape of feedstock solids without segregation problems (such as

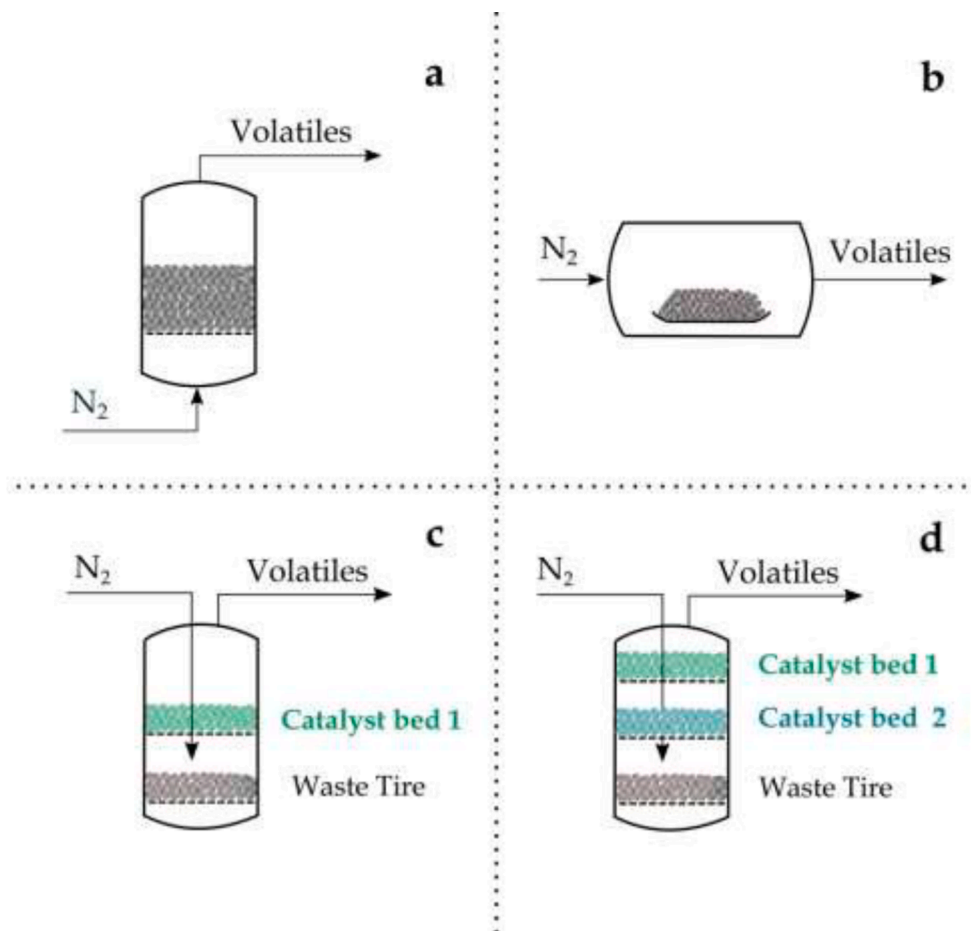


Fig. 6. Schematic diagram of fixed bed experimental equipment; vertical fixed bed (a), horizontal fixed bed (b), one-step catalytic bed [121,127] (c), and two-step catalytic bed [82] (d).

liquid-solid segregation and catalysts-raw feedstock segregation) [126]. The most significant advantage of the fixed bed reactor is that the catalyst bed can be added as required by the process due to its simple structure [82,121,127] (Fig. 6). In this respect, different reactor configurations have been used in tire catalytic pyrolysis. The simpler alternative is the use of the catalysts *in-situ* physically mixed with tire material [128–131], nevertheless, this strategy has some drawbacks including, higher coke deposition and the difficult separation of the catalyst and char at the end of the reaction [132]. However, the use of a second fixed reactor represents an interesting alternative (see Fig. 6c) [121,127,133–135]. It is worthy of note that this reactor system allows for independent temperature optimization in the pyrolysis and catalytic cracking steps, moreover the direct contact between the catalyst and waste tire impurities is also avoided. In addition, the use of two catalytic beds downstream of the pyrolysis reactor (Fig. 6d) has been also proposed [82]. Moreover, the pyrolysis target products could be obtained by placing different catalysts in the fixed bed [136].

Williams et al. [137] studied the effect of temperature and heating rate on the composition of pyrolysis products using a fixed bed reactor. The yield of tire char decreased with the increase of pyrolysis temperature, up to 600 °C, although the yield was still more than 35 wt. %. However, it was reported that the yield of char first decreased (500–600 °C) and then increased (600–900 °C) with a vertical fixed bed reactor [138], (Fig. 6a). With the temperature increase, the yield of char decreased using a horizontal fixed bed [69], (Fig. 6b). The high heating value of tire char varied from 11 MJ·kg⁻¹ without catalysts to 18 MJ·kg⁻¹ with a double catalysts bed. The specific surface area of tire char was 70.06 m²·g⁻¹ with one catalytic bed [121], (Fig. 6c). The yield of tire char reached nearly 45 wt. % with a single untreated char catalyst bed. Also, it appears that a decrease in sulfur content in the product oil was observed with single bed catalytic pyrolysis [127]. The influence of single and double fixed catalyst beds on the pyrolysis products of waste tires was studied [82], (Fig. 6d). Therefore, the number of catalyst beds has a significant effect on the yield of tire char. The yield of tire char varied from 36 wt. % (non-catalysts) to 43 wt. % (double catalysts bed). After the addition of the fixed catalyst bed, the yield of pyrolysis gas increased to 45 wt. % and was higher than that of thermal pyrolysis. The use of high carrier gas flow rates contributes to reducing residence time in the fixed bed and attenuating secondary reactions of pyrolysis volatiles that increase the yield of gaseous products or aromatics. This results in an increase in the production of the pyrolysis liquid phase, with a low oxygen content of 3.2 wt. % in the pyrolysis oil with a fixed bed such as that shown in Fig. 6b, and also produced an increase in the yield of tire char at 3.5 wt. % [139]. According to Cunliffe et al. [112], the yield of tire char remains fairly constant with a mean of 37.8 wt. % over a temperature range from 450 to 600 °C.

3.1.2. Fluidized bed

The fluidized bed is a reactor that uses gas or liquid to pass through a granular solid bed to make the solid particles rise in suspension and enables gas-solid reactions or liquid-solid reactions to take place. Compared with the fixed bed reactor, the advantages of the fluidized bed reactor include fast heating rate, operation under fast pyrolysis conditions [140], high heat utilization efficiency [141], short gas residence time [100,142], reduced extent of secondary reactions [143], and facilitates a continuous operational process with easy control [144–146]. The fluidized bed reactor is popular in the waste tire pyrolysis processing industry because it is a continuous operation, enables process scale-up, and produces a higher yield of oil [147,148]. However, there are also some problems with the fluidized bed such as high energy consumption [145], high investment cost, and the long cooling time needed for condensation of pyrolysis volatiles because of the high gas throughput. Due to the short residence time of the waste tire in fluidized beds, the tire char possesses a smaller specific surface area and less pore structure compared to char produced from fixed bed reactors. The fluidized bed is suitable for pyrolysis of waste tires with a small particle size

(0.1–2.0 mm) [145,149]. Tire char has exhibited an agglomeration phenomenon [150] observed from low-temperature pyrolysis in fluidized beds due to its incomplete pyrolysis [100] and short residence time. To completely pyrolyse waste tires, it is necessary to prevent low-temperature sintering (particle caking) and maintain stable operation of the fluidized bed in the process of waste tire pyrolysis [150]. The overall trend of char yield is decreasing with temperature increase using a fluidized-bed [100] (see Fig. 7). Moreover, fluidized bed reactors have excellent features for *in-situ* catalytic pyrolysis, enabling suitable gas-solid contact and the mixing regime ensuring high catalytic efficiency. In addition, operational strategies of catalyst circulation and continuous regeneration can be developed. Unlike the plastics catalytic pyrolysis process, fluidized beds have been scarcely used in catalytic tire pyrolysis. Williams and Brindle [151,152] studied the pyrolysis of waste tires using a fluidized bed reactor with in-line fixed bed catalysis. The use of a fluidized bed bench scale reactor with in-line catalytic cracking over HZMS-5 zeolite for the co-pyrolysis of waste tires and bamboo sawdust has also been proposed [153].

According to Raj et al. [154], the yield of tire char reached 45.5 wt. % at the conditions of, pyrolysis temperature, 475 °C, 0.3 mm particle size, and 17.5 g·min⁻¹ feed rate in a fluidized bed reactor, increasing the particle size to 0.71 mm produced the lowest yield of tire char at 24.5 wt. % at the same pyrolysis conditions of 475 °C and 17.5 g·min⁻¹ feed rate. They produced a char yield model which illustrated the relationship between char yield and input parameters. The pyrolysis of waste tires using a fluidized bed reactor has been studied by Dai et al. [100] and showed that an increase in temperature, residence time, and particle size led to a decrease in the yield of tire char. This result is similar to a model result in the reported literature [154]. It is reported that the sulfur content of tire char obtained from the fluidized bed pyrolysis was reported to be in the range of 2.1–2.3 wt. % and the ash content of tire char is about 10.6–11.3 wt. %. The specific surface area of tire char was reported to increase from 73 to 85 m²·g⁻¹ as the pyrolysis temperature was increased from 500 to 600 °C for the pyrolysis of tires in a fluidized bed reactor [155].

3.1.3. Conical spouted bed

The conical spouted bed reactor is similar to the conventional (bubbling) fluidized bed with the added advantage of inherent properties for handling sticky and irregular solids (such as waste tires) [156]. It has been observed by many researchers that the conical spouted bed has two advantages of short residence time and reduced secondary reactions of particulate matter. In addition, its design is simpler than that of the traditional fluidized bed due to there being no distribution plate and consequently, lower pressure drop in the pyrolysis chamber [157,158]. The high speed of movement of the gas in the conical spouted bed produces intense contact between the gas and solid phases, which helps to enhance the heat and mass transfer between the gas and solid phases and thereby improves the heating rate of the solids [159,160]. It is reported that a high yield of pyrolysis oil was obtained at low temperatures with the conical spouted bed reactor. However, the quality of the obtained tire char was improved at high pyrolysis temperatures [147]. A schematic diagram of a spouted bed reactor system is shown in Fig. 8 [147].

Lopez et al. [156] discussed the performance of the conical spouted bed reactor for waste tire pyrolysis under vacuum conditions. There was no reported agglomeration phenomenon of tire char when the conical spouted bed reactor was used which was attributed to the long residence time of pyrolysis at high temperature, however, the pores of the tire char were blocked and resulted in a low specific surface area. The yield of tire char obtained with the conical spouted bed was reported as 35 wt. % [161]. The sulfur content of tire char was high with a content of 3.68 wt. % [147], since, around 60 wt. % of the total sulfur contained in the waste tire was retained in the tire char at the pyrolysis temperature of 575 °C. The specific surface area of tire char obtained at 575 °C was 80 m²·g⁻¹. A similar conclusion is also reported in another research article

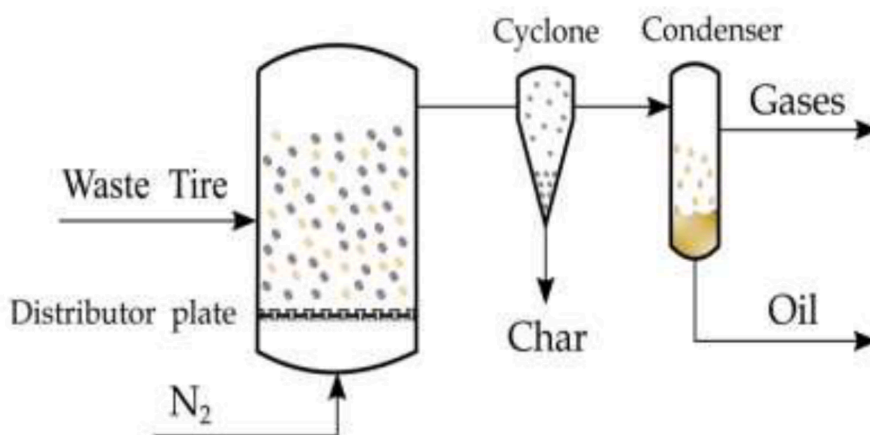


Fig. 7. Schematic diagram of fluidized-bed pyrolysis apparatus [100].

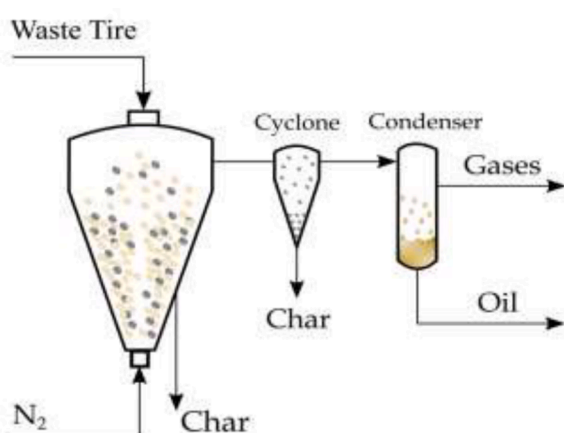


Fig. 8. Schematic diagram of the conical spouted bed bench scale process for waste tire pyrolysis [46,147].

[96], where it was reported that 33.7 wt. % of tire char was obtained using the conical spouted bed reactor. Tire char obtained with the conical spouted bed is regarded as poor quality and would require activation for its further application as activated carbon [162].

3.1.4. Rotary kiln reactor

The rotary kiln reactor has been widely applied for the pyrolysis of waste tires due to the adaptability of the reactor to cope with the variable shape and size of the waste tire in the pyrolysis operation. The rotary kiln drums are generally constructed to produce a horizontal or inclined cylinder rotating around its axis [163]. The rotary kiln reactor has been successfully applied in the field of pyrolysis of solid wastes because it allows good control of the process variables, especially waste solid residence time in the reactor [99,164,165]. However, there are some problems with the rotary kiln reactor, such as uneven temperature distribution and hysteresis, resulting in abundant heat loss and high energy consumption [166]. It is reported that tire char obtained from the rotary kiln reactor contains higher volatile matter, higher ash, and sulfur content, since the uneven temperature distribution results in unstable pyrolysis of the waste tire.

Ayanoglu et al. [167] reported a conversion of waste tire into tire char of about 35 wt. % using a rotary kiln reactor (Fig. 9). The tire char produced had a high heating value (HHV) and ash content of 23.69 MJ·kg⁻¹ and 10.35 wt. %, respectively. The specific surface area of tire char was reported to be very low, at 22.4 m²·g⁻¹. Increasing pyrolysis temperature from 700 to 900 °C, tire char yield was shown to decrease from 59.4 to 46.8 wt. % when one tonne of waste tire feedstock was

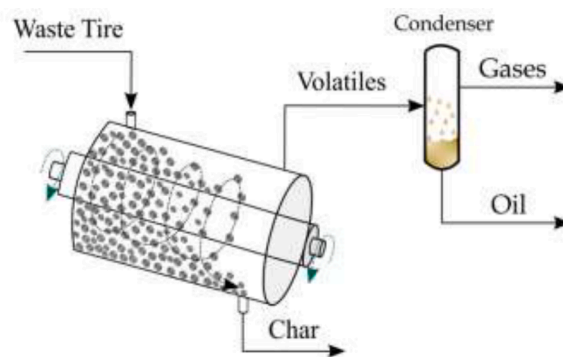


Fig. 9. Schematic diagram of the rotary kiln reactor pyrolysis system [167].

pyrolysed in a rotary kiln reactor with a capacity of 4.3 m³ [168]. The yield of tire char obtained was 41.2 wt. % [169] under a steam atmosphere with a rotary kiln reactor operating at high temperatures (850 °C). The sulfur content of tire char was reported as 3.0 wt. % and the specific surface area of the tire char was 40 m²·g⁻¹, which was higher than that of Ayanoglu, at the 22.4 m²·g⁻¹ [167] due to the high ash content (10.35 wt. %) in the tire char. It has also been shown that the specific surface area of tire char obtained from a rotary reactor increased significantly with increasing pyrolysis temperature [170].

3.1.5. Auger reactor

The auger type reactor for pyrolysis of waste tires has become more and more popular in recent years due to its higher heat transfer efficiency, better tire conversion rate, low carrier gas demand, low energy requirements, and other advantages. An advantage of the auger reactor is the low specific size and ease of portability, therefore, enabling its use where the waste is generated or concentrated. The portability of the auger reactor is conducive to reducing the costs associated with transportation, management, and logistics of the waste. The tire char yield is similar in both fixed bed and single-auger reactors, at approximately 38 wt. % of the raw tire material. However, the residence time of material in an auger reactor is shorter than that in a fixed bed. Some studies have considered the single-auger reactor for conducting the pyrolysis of waste tires. According to one study, the tire char yield reached 40.6 wt. % at a pyrolysis temperature of 600 °C and 3.7 min residence time. The volatile matter yield in the tire char is reported to be lower than 5.0 wt. % with a single-auger reactor [171]. This reactor could improve the total conversion with a short solid residence time (<1.5 min). Another study reported that the tire char yield reached 40.5 ± 0.3 wt. % at 550 °C, with the maximum sulfur content in tire char of 2.6 wt. % [172] with a

single-auger reactor (Fig. 10a). The twin-auger reactor is effective for the intermediate pyrolysis of waste tires, obtaining more yield of tire oil, and reduced tire char yield. The tire char yield ranged from 39.24 wt. % at a pyrolysis temperature of 475 °C to 46.55 wt. % at 400 °C with a twin-auger reactor [173] (Fig. 10b). The sulfur content in tire char obtained from a twin-auger reactor was shown to be 3.6 wt. % with a char specific surface area of 57.0 m²·g⁻¹ [174]. It was also reported in the literature that the tire char yield obtained from a twin-auger reactor is higher than that obtained with a single auger reactor, however, the HHV, volatile matter, and S_{BET} of the tire char was lower than that obtained with single auger reactor. From the perspective of tire char, a twin-auger reactor for tire pyrolysis is better than that of a single auger reactor. The use of a single auger reactor may lead to material accumulations or plugging because of the simple conveyance of the tire feedstock via screw feeding and small size feedstock. However, the twin-auger reactor could promote a constant feeding of the feedstock, and in addition, leads to better mixing effectiveness among the particles of the feedstock and with other materials when granular solids are used as heat carriers [175].

Pyrolysis reactors have different advantages and disadvantages, and application scopes. The method of heat and mass transfer has a significant effect on the distribution of pyrolysis products and their quality. Thus, fast pyrolysis conditions, i.e., high heating rates and short residence times of volatiles, lead to a high yield of oil products and lower yields of gases and tire char, which is the typical situation in fluidized and spouted bed reactors. However, the operation under slow pyrolysis conditions promotes secondary reaction with the subsequent increase of gaseous products and char, and a reduction of oil yield [21,22], with fixed beds being the most common slow pyrolysis technology. Table 2 shows that the quality of tire char produced is significantly different with various pyrolysis reactors. This phenomenon occurs because different pyrolysis reactors are suitable for different shapes and sizes of the waste tire and that the pyrolysis conditions of pyrolysis reactors are different. Thus, fast heating of tire particles promotes a fast rubber devolatilization and rapid release of pyrolysis volatiles. However, under slow pyrolysis conditions, volatiles formation takes place over a longer time period and these products require a long time to leave the tire particles. This increase in residence time promotes degradation intermediates to form inside tire particles and favors carbonization of volatiles by secondary reactions with the subsequent increase in tire char yields and the ratio of pyrolysis char to original carbon black in the product tire char. Compared with the fixed bed reactor, the fluidized bed, rotary kiln and spouted bed reactors could operate at an industrial scale with continuous operation and waste tire feeding. However, there are also some problems needed to be solved for the development of a

continuous feed pyrolysis process which include: (i) improving the gas sealing performance of the feeding system; (ii) isolating the reactor and the feed system effectively; (iii) operating the reactor safely and stably; (iv) optimizing the process parameters. In the development of the waste tire pyrolysis process, selecting an appropriate pyrolysis reactor cannot only reduce the investment cost but also increase process throughput.

3.2. Pyrolysis processes

To change the product distribution, improve the quality of pyrolysis products, or gain operational advantages, different alternative processes to conventional thermal pyrolysis have been proposed in the literature. These commonly used pyrolysis processes for treatment of the waste tires are mainly vacuum pyrolysis, pressurized pyrolysis, microwave pyrolysis, plasma pyrolysis, hydrogenation pyrolysis, co-pyrolysis, and catalytic pyrolysis. The mechanism by which the products of pyrolysis are improved in relation to these pyrolysis technologies will be different.

3.2.1. Vacuum pyrolysis

The vacuum pyrolysis process has been developed and widely used in the treatment of, for example, waste straw, plastic, and oil sludge [181–183]. The vacuum pyrolysis of solid wastes is a pyrolysis technology that uses a vacuum pump to generate negative pressure in the pyrolysis reactor, release volatiles off solid wastes and reduce the residence time of volatiles in the pyrolysis reactor. Vacuum pyrolysis not only reduces the possibility of secondary reactions of pyrolysis volatiles but also has a significant influence on the yield and distribution of pyrolysis products [93,184]. Interestingly, a positive effect of the lower yield of organic compounds attached to the tire char has been reported [93,156]. Moreover, the operation under vacuum conditions reduces the inert gas flow rate requirements and accelerates the tire degradation rate [156]. In addition, low-temperature vacuum pyrolysis has lower tolerance requirements related to the ability to withstand temperature and the construction materials of the pyrolysis equipment [185]. According to Lopez et al. [156], a slight reduction in tire char yield was obtained from vacuum pyrolysis (253 mbar), where 33–34 wt. % yield of tire char was reported with a specific surface area of 96 m²·g⁻¹ (pyrolysis temperature 425 °C), which was higher (46 m²·g⁻¹) than that obtained under ambient pressure. Compared with the properties of pyrolysis products under atmospheric conditions, vacuum pyrolysis could prevent the pores of the tire char from being blocked and thereby improve the surface properties of tire char. This positive effect on the quality of tire char is due to the short residence time of pyrolysis volatiles on the surface of the tire feedstock during the reaction process. Results from vacuum pyrolysis of tire rubber showed the production of a good quality

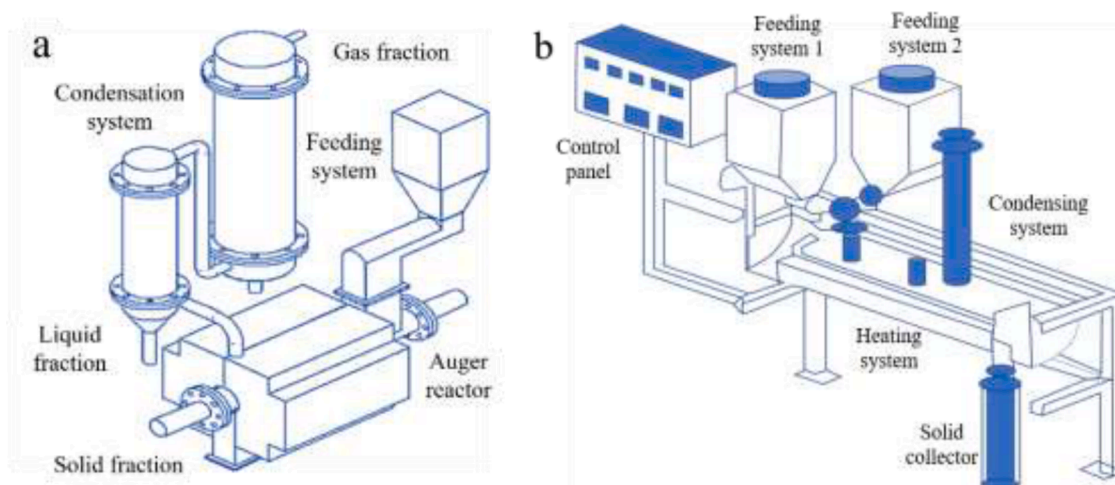


Fig. 10. Experimental set-up of the single auger reactor (a) [172] and twin-auger reactor (b) [173].

Table 2
Comparison of the advantages and disadvantages of waste tire pyrolysis reactor designs.

Pyrolysis reactor	Fixed bed	Fluidized bed	Conical spouted bed	Rotary Kiln bed	Auger reactor
Reactor scale	H: 11.45-30 cm D: 2.0-15.0 cm	V: 210-1766 ml D: 5.0-30.0 cm	H: 34.0 cm conical section H: 20.5 cm Angle: 28 ° upper D: 12.3 cm bottom D: 2 cm	H: 21.3-660 cm D: 15.0-220 cm V: 3.76 dm ³ -25 m ³	Laboratory mall-scale instruments
Tire size	0.25-3.00 mm	0.14-10 mm	1-2.0 mm	0.3-4.0 cm	2-5 mm
Conditions (M, T, H1, N, RT)	30-50 g, 400-850 °C, 5-25 °C/min, 25-100 mL/min, 10-120 min	0.6-3.0 kg/h, 350-805 °C, -, 25-100 mL/min, 1-3.0 s	0.3-3.0 kg/h, 400-600 °C, -, 3.0-9.5 L/min, 20 ms	0.04-5.0 kg/h, 400-1100 °C, -, 3.0-9.5 L/min, -, speed rotation:0.5-3.0 rpm	1.0-6.0 kg/h, 400-600 °C, 5-20 °C/min, 0.15 -11.4 L/min, 3.7-120 min
Advantage	Low back mixing, simple structure, small mechanical loss of catalysts. Realizing multiphase reaction process. Beneficial to target products.	High heating rate, short gas residence time, high thermal utilization rate, small secondary reaction, easy industrial scale-up.	Handle highly sticky and irregular materials. Flexible operating conditions. Continuous carbon black removal. Simple process design.	Wide adaptability to material shape and size.	Higher heat transfer efficiency, better conversion rate, short residence time, low specific size and ease of portability
Disadvantage	Long time to start and stop, high energy consumption, low work efficiency, uneven distribution of pyrolysis products.	High energy consumption, high investment cost, long cooling time of volatiles.	Small specific surface area of tire char. Uneven of solid residence time due to rapid circulation of solid and agitation	Uneven and lagging of temperature distribution, large heat loss, high sulfur content of pyrolysis oil, low flash point.	Material accumulations in reactor, only suitable for small size feedstock.
Oil (wt.%)	42-58	25.3-44.5	53.9-58.0	28-37	41.8-46.5
Gas (wt.%)	4-11	16.18-46.0	3.6-10.2	20-31	11.3-18.1
Char (wt.%)	38-47	24.50-45.5	35.9-37.9	35-41	39.0-42.6
Ultimate analysis of tire char (air dry basis)					
C (wt.%)	74.60-82.1	88	86.5-86.9	77.4-89.86	74.7-85.4
H (wt.%)	1.06-1.0	9.5-11	0.7-0.8	0.4-3.14	0.8-1.7
N (wt.%)	0.49-1.0	0.29-0.41	0.3-0.5	0.29-1.2	0.4-0.7
S (wt.%)	2.46-2.54	2.1-2.3	2.1-3.6	1.72-2.28	2.0-2.6
O (wt.%)	2.5-3.5	-	-	3.1-4.8	< 0.1
Proximate analysis of tire char (air dry basis)					
M (wt.%)	-	-	-	0.50	0.45-4.3
V (wt.%)	-	-	-	74.09	1.33-6.3
FC (wt.%)	-	-	-	15.06	78.1-81.6
Ash (wt.%)	8.24-20.4	10.6-11.3	7.1-7.3	9.0-17.2	11.6-20.5
HHV (MJ/kg)	11-18	-	-	23.69	25.5-30.6
Char S _{BET} (m ² /g)	40-230	73-85	46.5-116.3	22-40	57.0
Refs.	[121,139,170,176,177]	[149,154,155,178]	[156,159,179,180]	[48,139,167]	[171-174]

H: Height; D: Diameter; V: Volume;

M: experimental mass; T: Temperature; H1: Heating rate; N: Nitrogen flow rate; RT: Residence time; - not described in the reference text.

tire char with a small amount of carbon deposition formed on the surface of the char [186]. Pyrolysis of truck tire under vacuum conditions (total pressure lower than 100 mbar) produced a tire char with a specific surface area of 95 m²·g⁻¹ with 0.7 wt. % ash and 0.5 wt. % sulfur contents [187]. However, an issue that exists with vacuum pyrolysis is the low efficiency of heat transfer within the reactor. Therefore, increased heat input is required to operate at full load [188]. The vacuum pyrolysis technology of waste tires has obvious advantages of high efficiency and safety, but its disadvantages are the low yield of tire char and high content of heavy oil compounds in the liquid products.

3.2.2. Pressurized pyrolysis

Opposite to vacuum pyrolysis, the pressurized pyrolysis of solid wastes has been investigated. The pressurized pyrolysis of solid wastes involves addition of a pressure balancer (back pressure valve) after the pyrolysis reactor to adjust the internal pressure of the pyrolysis reactor to be higher than ambient pressure. The solid wastes are pyrolyzed in this high-pressure environment. Pressurized pyrolysis inhibits the diffusion movement of volatiles, results in the volatiles not immediately leaving the solid wastes, and increases the residence time of the volatiles in the pyrolysis reactor and the probability of secondary cracking reactions. The influence of pressurized pyrolysis has been reported in relation to the pyrolysis products of, for example, biomass [189] and coal [190] where it was shown that increased pressure resulted in an increased yield of char. This advantage reported for biomass and coal pressurized pyrolysis has also been reflected in waste tire pyrolysis. The yield of tire char increased 10.40% when the pressure of the pyrolysis

system was varied from ambient to 2.0 MPa at a pyrolysis temperature of 600 °C. Compared with the tire char obtained from ambient pressure, the pressurized pyrolysis tire char has a characteristic of melting and cross-linking, therefore, the specific surface area of tire char derived from pressurized pyrolysis was smaller than that of tire char obtained from ambient pressure. Wang et al. [191] have carried out research on pressurized pyrolysis tire char, and reported on the carbon crystal form and pore size of the pressurized pyrolysis tire char. It was confirmed with Raman spectrometry that the pressurized pyrolysis tire char has a tendency towards graphitization. The pressurized pyrolysis tire char has a high selectivity and catalytic effect towards the pyrolysis oil of waste tires [191]. Although Ma et al. [192] studied the pressure influence on waste tire pyrolysis, the tire char obtained from pressurized pyrolysis was not investigated.

At present, there are relatively few studies on the pressurized pyrolysis of waste tires, but the advantages of its treatment are significant. The pressurized pyrolysis of waste tires increases the yield of tire char and pyrolysis oil and reduces the yield of pyrolysis gas. The process is cleaner and has fewer pollutant emissions. However, the mechanism of pressurized pyrolysis of waste tires has rarely been reported, which should be part of future research work. The pressurized pyrolysis of waste tires is still in the laboratory stage and although higher value products are easier to be obtained, few industrial applications have been reported. If the target products of waste tire pyrolysis are high-yield tire char and high-quality pyrolysis oil, the pressurized pyrolysis can be considered a priority treatment method.

3.2.3. Microwave pyrolysis

Microwaves refer to electromagnetic waves with a frequency of 300 MHz - 300 GHz and a wavelength of 1-100 cm [193]. The microwave is a process whereby materials absorb the microwave energy and convert it into heat energy [194], this property enables the process to be developed for the pyrolysis of waste tires. The distinct characteristics of microwave pyrolysis include high selectivity in relation to the pyrolysis oil components (limonene, 23.4%) [195], gas components (H_2 , 54.52%) [196] and high efficiency in the wastes pyrolysis treatment process [197]. In addition, this heating method allows for homogeneous heat distribution in the reactor [195,196]. Microwave pyrolysis is suitable for materials with low thermal conductivity such as waste tires. The presence of the reinforcing carbon black material in the tire rubber, which is a low thermal conductivity material, could enhance the transfer of the microwave energy into the rubber to promote rubber pyrolysis and generate more tire char [198,199]. The effect of microwave power on the pyrolysis products of waste tire powder was reported in various literature reports [199–201]. The degree of pyrolysis of the waste tire powder increased with the increase of microwave power. At 500 w of microwave power, the maximum conversion rate of the waste tire was realized, resulting in a product yield of 45.0 wt. % oil, 18.5 wt. % gas, and 36.5 wt. % char. The performance of waste tire pyrolysis products with microwave-assisted pyrolysis has been investigated [202,203]. The results showed that low amounts of organic substances were present and blocked the pores of the tire char but did not affect the direct utilization of the product tire char. The content of sulfur in the tire char was about 50% of the initial sulfur present in the feedstock tires, which is in agreement with results reported elsewhere in the literature [155]. The char obtained from the waste tire has a higher LHV ($33 \pm 3 \text{ MJ}\cdot\text{kg}^{-1}$) [204,205]. It has been reported that the apparent density of the tire char was in the range of $0.40\text{--}0.56 \text{ g}\cdot\text{mL}^{-1}$, which was higher than an exfoliated graphite but lower than graphite ($2.25 \text{ g}\cdot\text{mL}^{-1}$) [206]. Compared to catalytic pyrolysis technology, microwave pyrolysis could reduce the occurrence of secondary reactions. Microwave pyrolysis technology does not require any pretreatment of the tire feedstock, even including crushing and grinding, that is, the waste tire can be used directly. At present, this technology for waste tires treatment is only at laboratory scale experiments.

Microwave pyrolysis has a thermal effect on the pyrolysis of waste tires, as well as a non-thermal effect caused by the characteristics of the microwave itself and the action of the microwave field. Compared with the traditional pyrolysis method, microwave pyrolysis not only shortens the pyrolysis time and saves energy, but also reduces the cost of waste tires treatment. It has many advantages that traditional pyrolysis technology does not have. However, the problems of microwave pyrolysis include the high cost of large-scale continuous production of microwave energy required for the pyrolysis equipment and the incomplete understanding of the mechanism of microwave pyrolysis. Although microwave pyrolysis of waste tires is not the mainstream technology in the market, the development of a large-scale microwave pyrolysis reactor is a necessary step to promote an industrial scale application. In addition, the microscopic mechanism of microwave pyrolysis, that is the mechanism of the thermal effect and non-thermal effect on waste tires treatment, should also be considered in future research work.

3.2.4. Plasma pyrolysis

Plasma is the fourth state of matter except for solid, liquid, and gas, which is a state of matter formed by positive and negative ions generated after the atoms are ionized. Plasma technology involves the creation of a sustained electrical arc by the passage of electrical current through a gas. The plasma pyrolysis process has received attention because of a substantial number of advantages of the technology, such as small space volume, high treatment rate, quick start and stop, and completely decomposing material into small molecules. According to experimental results, thermal plasma pyrolysis has been investigated as a promising method of treating waste tires for energy and resource recovery [207,

208]. Huang et al. [209] have tested the characterization of the gas and char products derived from waste tires obtained from thermal plasma pyrolysis and found that the main components of the gas products are H_2 , CO, CH_4 , C_2H_2 , and C_2H_4 . The combustion heating value of the tire pyrolysis gas was about $5\text{--}9 \text{ MJ}\cdot\text{Nm}^{-3}$. The tire char yield varies from 39 to 69 wt. %, and contains more than 16 wt. % ash content, 80 wt. % carbon content, and 2.7 wt. % sulfur content. The specific surface area of tire char is about $70 \text{ m}^2\cdot\text{g}^{-1}$. The tire char analysed by X-ray photoelectron spectroscopy, revealed that tire char has a mainly graphitic carbon structure. TA later report by Huang et al. [210] showed that increasing the radio-frequency power (1600-2000 W) increases waste tire pyrolysis conversion (34.4-78.4 wt. %) and decreases tire char yield (21.6-65.6 wt. %). The products of waste tires obtained from plasma pyrolysis are mainly gas and tire char. This technology could completely deal with waste tires with no need for the condensation process to recover pyrolysis oil. However, the quality of tire char from plasma pyrolysis technology was poor, the specific surface area was small and the ash content in tire char was high. Compared with conventional pyrolysis technology, the plasma pyrolysis of waste tires has some disadvantages; in the plasma pyrolysis process, due to high voltage discharge, plasma is unstable and it is necessary to prevent explosion accidents caused by sparking; plasma pyrolysis will increase equipment cost and results in a consequent additional increase in the cost of waste tires treatment. The plasma pyrolysis of waste tires has been studied mainly on the laboratory scale, and no industry reports have been found. Plasma pyrolysis is a promising treatment method for waste tires treatment, but it is not the main treatment method. Although the plasma pyrolysis technology of waste tires is currently only investigated at the laboratory scale, there is still much research work to be explored, such as the mechanism of plasma pyrolysis of waste tires, and the combined action mechanism of plasma autocatalysis and high temperature.

3.2.5. Hydro-pyrolysis

Hydro-pyrolysis is a mature technology and is widely being used in terms of petroleum refining [211,212]. Hydro-pyrolysis could not directly stabilize the pyrolysis oil derived from solid wastes, but it has the effect of altering pyrolysis volatile hydrocarbons to generate more saturated hydrocarbons. To improve the quality of the pyrolysis oil produced from waste tires and meet the characteristics required for fuel oil applications, some researchers have explored the chemical structure characteristics and application feasibility of the recombination products obtained from waste tire hydrogenation pyrolysis [213]. The hydro-pyrolysis process is a simple and effective method for waste tire clean conversion into useful products. It can adjust the yield and quality of the pyrolysis oil, gas, and tire char products. The hydro-pyrolysis of waste tires mainly affects the quality of the liquid (processing heavy oil into light oil) and gas phase (increasing the yield of non-condensable gases such as H_2 , CH_4 , and C_2H_4) products [214]. However, this process has little influence on the yield of tire char. Compared with direct pyrolysis of the waste tire, some advantages of waste tire hydro-pyrolysis include decreasing the energy consumption, reducing secondary condensation as well as polymerization of the oil. This process is beneficial to increase the yield of pyrolysis oil and gas, however, the yield of tire char is reduced [215]. For example, the influence of the hydro-pyrolysis process on the product distribution of waste tires was investigated [216], and the yield of tire char was 33.83 wt. % at a process temperature of $430 \text{ }^\circ\text{C}$, which was lower than that of other reported pyrolysis processes. The changes in the hydro-pyrolysis products of waste tires using a fixed bed reactor to adjust the pyrolysis process were studied [217]. The specific surface area of tire char that was obtained from hydro-pyrolysis varied from 50 to $70 \text{ m}^2\cdot\text{g}^{-1}$ and the ash content of the char was close to 12 wt. % resulting in the low yield of tire char obtained from waste tires hydro-pyrolysis. The purpose of hydro-pyrolysis of waste tires was to obtain high-quality pyrolysis oil and gas, not tire char. Compared with conventional tire pyrolysis technology, hydro-pyrolysis has higher requirements for reaction

equipment, and higher investment costs, and the quality of the tire char is relatively poor.

3.2.6. Co-pyrolysis

Co-pyrolysis technology is a technology in which two materials of different compositions can complement each other's advantages during the pyrolysis process, have a synergistic effect and improve the quality of pyrolysis products. The synergistic co-pyrolysis of waste tires with coal [218,219], cooking oil [220], plastic [221], and biomass has been studied widely, with an emphasis on liquid yield and quality [153,222,223]. Since the waste tire rubber and especially waste plastics are rich in hydrogen, co-pyrolysis with coal, biomass, and other materials has potential, since the waste tire acts as a hydrogen donor and improves the quality of the pyrolysis volatiles and increases the yield of pyrolysis oil [224,225]. The pyrolysis oil obtained from the co-pyrolysis of the waste tire with biomass represents a promising alternative to fossil fuels. The pyrolysis oil obtained from biomass cannot easily be directly used as fuel oil because of its high oxygen content, low chemical stability and high corrosion potential related to the presence of organic acids [226]. It is reported that biomass and waste tire co-pyrolysis produced a high-quality oil in terms of polycyclic aromatic hydrocarbon content [227]. In addition, a significant reduction of sulfur content in the product oil is achieved from the co-pyrolysis of tires and biomass. According to the analysis of product composition and yield, the results show that there exists a synergistic effect in the co-pyrolysis of waste tires and other materials. In the initial and final stages of the pyrolysis process, biomass acts as an activator and promotes thermal decomposition of the waste tire with a significant synergistic effect [228]. Onay et al. [229] studied the effect of co-pyrolysis of lignite and waste tire on pyrolysis products under different pyrolysis temperatures and material ratios (waste tire: lignite ratio) using a fixed bed. The TG curves obtained are illustrated in Fig. 11. No matter which ratio was used, the yield of char from the tire/lignite mixture was higher than that obtained from only the waste tire. With the increase in temperature, the yield of tire char from the mixture or waste tire only decreased.

Comparing the properties of the co-pyrolysis products of bituminous coal and waste tire, Bicakova et al. [218] found that the co-pyrolysis of the waste tire and coal have a synergistic promoting effect. The yields of pyrolysis products are presented in Fig. 12. Under suitable conditions, the gas products had high hydrogen and methane volumetric concentrations, of more than 60% and 20% respectively, and the content of aromatic hydrocarbons in the pyrolysis oil was low. The yield of tire char from the raw mixture (waste tire and coal) was higher than that from only waste tire pyrolysis. The experimental process of co-pyrolysis and

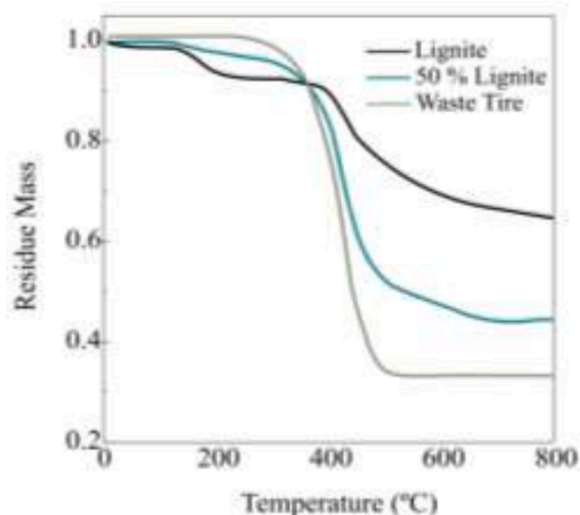


Fig. 11. TG analysis of waste tire, lignite and tire/lignite mixture (5/5) [229].

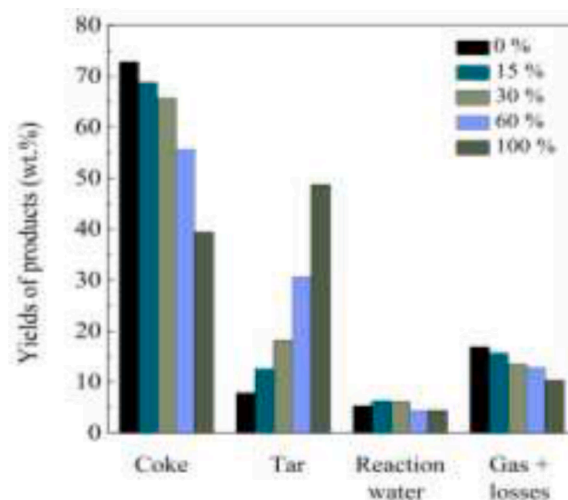


Fig. 12. Yields of pyrolysis products from lignite (black columns), tire: lignite mixture (wt.%), and waste tire at different ratios of waste tires and coal [218].

gasification of coal and waste tire for power generation were reported in the literature [230]. The emissions of CO, CO₂, SO₂, and NO_x from the combustion of the syngas produced from co-gasification of the mixture of tire and coal decreased by 3.4, 23.28, 22.9, and 0.85% respectively when using a 1:1 mixture ratio (coal/waste tire). Biomass/tires co-pyrolysis has been widely reported, but only limited studies have been carried out in continuous pyrolysis reactor units. A screw kiln reactor was used for the continuous co-pyrolysis of 5 kg·h⁻¹ of forestry waste and tires [227], an oil with good quality and stability was obtained, moreover, the obtained char showed a heating value of around 30 MJ·kg⁻¹.

Wang et al. [153] studied bamboo sawdust and tire co-pyrolysis and in-line catalytic cracking in a reaction unit made up of a fluidized bed and a fixed bed reactor. The increase of tire content in the feed promoted char yield, moreover, the production of valuable chemicals such as BTX (benzene, toluene, xylenes) was also improved. Recently, the continuous pyrolysis of pine wood and waste tire in a conical spouted bed reactor was investigated [231], co-pyrolysis produced a liquid with a lower oxygen and water content and a solid product with lowered ash content. The co-pyrolysis of the waste tire and other materials has obvious advantages on co-pyrolysis gas and oil, but its disadvantages in relation to the product char should also not be ignored. Although char yield from the waste tire co-pyrolysis process is higher than that of bio-char [231] or plastic char [232] and lower than that of tire char, the tire char has a relatively low carbon content due to the presence of the co-feedstock and high ash content [233–235]. However, the char yield from the co-pyrolysis of waste tires with coal was lower than that from coal pyrolysis [218]. The quality of tire char from the co-pyrolysis process was poor, where the ash content reached 8.68 wt. % [176,221]. Wang et al. [236] reported that the yield of co-pyrolysis char from waste tires and pine bark was lower than that of waste tire produced char but higher than that from pine bark. The specific surface area of the product char varied from 40 to 110 m²·g⁻¹. Compared with the research reports of other researchers, the study of Wang et al on the co-pyrolysis synergistic mechanism of waste tires and pine bark is relatively in-depth and thorough. Comparing the experimental results of blends with the results of separate pyrolysis of different raw materials under the same pyrolysis conditions, the synergistic effect of the co-pyrolysis was calculated to quantify the synergistic effect. The results showed that a blend of waste tires and pine bark increased the evolution of syngas. However, the influence of co-pyrolysis on the properties of char was not discussed. The elemental composition of solid wastes is different, and consequently, the quality, ash content, and specific surface area of tire char produced by the co-pyrolysis process are different.

It can be concluded from the above cases of co-pyrolysis research that the synergistic mechanism of different substances involving waste tires co-pyrolysis is different. The different co-pyrolysis mechanism leads to the production of a tire char with different morphology. The results reported by different authors are significantly different, and the insights into the co-pyrolysis of waste tires and other materials are limited. The co-pyrolysis of waste tires and other waste materials has different effects on tire char, but the addition of most materials to the pyrolysis of waste tires could reduce the quality of tire char and increase the ash content.

3.2.7. Catalytic pyrolysis

Obtaining the target products from non-catalytic pyrolysis of waste tires requires high temperature, long duration, and high energy consumption. The addition of catalysts to the waste tire pyrolysis process reduces the activation energy of pyrolysis reactions, promotes the fast pyrolysis of the waste tire, affects the product composition, increases the yield of low molecular weight hydrocarbons, and effectively improves the distribution of pyrolysis products [47,94,237]. Compared with non-catalytic pyrolysis, the main advantages of catalytic pyrolysis are: (i) promoting the pyrolysis efficiency; (ii) reducing the reaction temperature and activation energy of pyrolysis; (iii) improving the quality of pyrolysis products and the yield of valuable chemicals [238,239]. The yield, composition, and quality of pyrolysis products could be promoted and more valuable chemical products obtained with the use of catalysts in the waste tire pyrolysis process [240,241]. When the catalysts and waste tires are mixed, utilization of catalysts is not only conducive to the conversion of heavy oil to light oil [242] but also encourages the recombination of the surface chemical structure of tire char and reduces the content of functional groups of impurities on the surface of the tire char [127,243]. The commonly used catalysts for the catalytic pyrolysis process are zeolites, alkaline compounds (e.g. KOH, Ca(OH)₂, and Al₂O₃) [34], ores, and steel slag [159,244]. Zeolite catalysts have become popular due to their unique pore and channel structure, which may be loaded with a highly active metal to obtain higher quality products. Moreover, most alkaline compounds with a high specific surface area could be used as catalysts. Cheap minerals (e.g. dolomite) are widely investigated since they contain a variety of catalytic elements [245,246].

Zhang et al. [247] studied the influence of nickel catalysis on the pyrolysis gas yield from waste tires using a two-stage pyrolysis-catalytic steam reforming process. Nickel as a catalyst promotes the secondary reactions of pyrolysis volatiles, at the same time, carbon deposition on the catalyst produced and blocked the pore structure on the surface of the catalyst. The ratio of catalyst support material and active metal plays an important role in the yield of carbon deposition on the surface of the catalyst. When Al₂O₃ and SiO₂ served as the support material for the nickel catalyst, and the ratio of carrier and catalyst changed from 1:1 to 2:1, the content of carbon deposition on the surface of the catalyst decreased from 19.0% to 13.0%, and more than 95% of carbon deposition was in the form of filamentous carbon nanotubes. Osorio-Vargas et al. [40,248,249] analyzed the performance of different supported noble metal catalysts based on Ni, Pd, Pt, and Co in waste tire pyrolysis performed in a Py-GC/MS instrument. Interestingly, these catalysts showed a remarkable selectivity for the production of valuable aromatic compounds such as benzene, toluene, xylenes, or cymene. The influence of catalysts on the batch pyrolysis of waste tires has been studied in the literature [243]. The results showed that ZSM-5, Al₂O₃, CaCO₃, and MgO can cause the delay in the initial degradation temperature, where it was shown that the initial degradation temperature (329 °C) of tire rubber increased to 371 °C in the presence of CaCO₃, 340 °C with Al₂O₃, 402 °C with ZSM-5, and to 371 °C with MgO. The presence of CaCO₃ and MgO reduced the pyrolysis activation energy from 246.89 kJ·mol⁻¹ in the absence of the catalyst material to 121.82 kJ·mol⁻¹ and to 128.34 kJ·mol⁻¹, respectively. The high acidity of the zeolite catalyst promoted the pyrolysis of the waste tire more thoroughly. The yield of char

obtained from the waste tire pyrolysis catalyzed by zeolite was low due to the mix of zeolite catalysts and waste tires. Catalysts are beneficial to the recombination of tire char chemical structure. Fig. 13 shows the effect of catalysts on the product yield and HHV of the liquid and solid products. In Fig. 13a, the yield of char obtained from zeolite with added Ca(OH)₂ was higher than when no catalyst was added. While the yield of char from added Al₂O₃ was lower than in the non-catalyst experiment (Fig. 13b). The HHV of the solid char is related to the product char yield (Fig. 13b and 13c).

There are some disadvantages of incorporating catalysts *in-situ* in the waste tire pyrolysis process, for example, some catalysts have high costs and are not easy to be separated from tire char after the pyrolysis process. In the past, most of the catalytic pyrolysis of waste tires was carried out after blending the waste tire with catalysts. This blending process of waste tires with catalysts improved the tire oil quality and the yield and quality of pyrolysis gas but decreased the quality of tire char. The catalytic pyrolysis behavior much depends on the contact of catalysts and tire pyrolysis volatiles. Because the particle size and shape of the waste tire and catalysts are much different, their contact with any degree of confidence remains unknown. Also, a major problem that existed in this type of catalytic pyrolysis is how to extract and recycle the catalyst from the catalyst/char mixture after reaction. At present, it is difficult to find literature on the recovery of the catalyst from the product tire char and the presence of used catalyst also leads to poor quality tire char. Moreover, the direct contact of the catalysts with the waste tire impurities could provoke a fast catalyst deactivation and thereby shorten the lifetime of the catalyst. In this regard, the use of the catalysts *ex-situ* represents a more effective alternative. However, the use of catalysts at full scale requires a suitable process to overcome fast catalyst deactivation and requires the implementation of processes with continuous catalyst regeneration. In this scenario, the increase in material and operational costs should be balanced with the improvements in product yields and their quality in relation to thermal pyrolysis to determine the full potential of catalytic pyrolysis [47].

However, there are some interesting studies for enhancing the quality of pyrolysis oil and gas that will not decrease the quality of tire char. Fengchao et al. [24] reported a promising pyrolysis process in which waste tires were placed in a two-stage fixed bed separately. The pyrolysis tire char was prepared in the lower fixed bed reactor and used as a catalyst for catalytic cracking of the volatiles from the upper fixed bed. In this way, three advantages were obtained: (i) the volatiles from the upper fixed bed were cracked into light oil with a high content (high content of single ring aromatics) and light gas with a high yield; (ii) the tire char was not influenced by the presence of the catalysts in the lower bed; (iii) after the catalytic process, the yield of tire char obtained from the lower fixed bed increased; this was because the carbon deposits generated on the surface of tire char resulted in an increased carbon content and decreased ash content. Another process for improving the quality and yield of pyrolysis oil and char was also reported involving pressurized catalytic pyrolysis of waste tires where it was shown that the yield of tire char increased and the carbon content of the char increased at high pressure [191]. At the same time, pressurized catalytic co-pyrolysis of waste tire and oil sludge [251] or pine sawdust [252] using a two-stage fixed bed reactor with bottom ash obtained from oil sludge combustion, showed that the produced tire char yield increased and ash content decreased. Comparing the position of catalysts in the catalytic pyrolysis processing of waste tires, as either blending, or stratification of the catalysts, it can be shown that the stratification method improves the quality of pyrolysis products without reducing the quality of tire char. This two-stage catalytic pyrolysis process solves the problem of catalytic recovery. However, there are few studies on the fluid mechanics, turbulence, and local heat/mass transfer of waste tires catalytic pyrolysis.

Much literature on the catalytic pyrolysis of waste tires has been reported and clearly it has been shown that different catalysts have different catalytic effects. However, most researchers focus on the

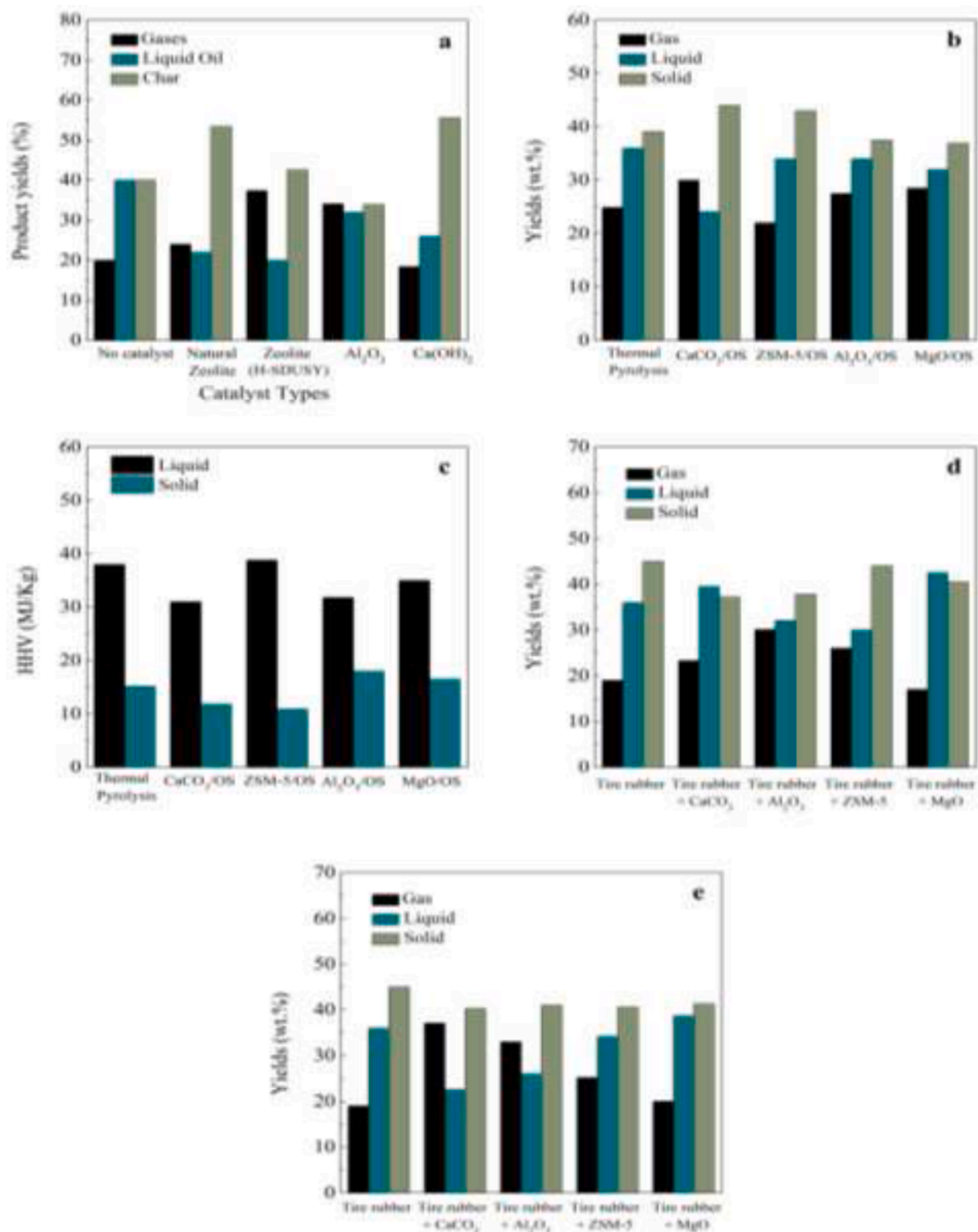


Fig. 13. Effect of catalytic and non-catalytic pyrolysis on products yields. (a): catalysts were in contact with tires [250], (b) and (c): catalysts were not in contact with tires [82], (d): catalysts were covered on tires, and (e): catalysts were placed over tires [243].

quality improvement of waste tire pyrolysis oil and gas, seldom was any attention placed on the quality and characteristics of the tire char from the catalytic pyrolysis, an aspect that should be studied more in future work.

Table 4 summarizes the reaction mechanism of tire pyrolysis and also compares the advantages and disadvantages of different waste tire pyrolysis processes. According to the target pyrolysis product, the accurate selection of suitable pyrolysis technology and the process type could be conducive to saving resources, reducing energy consumption, and improving the quality of the products. An individual pyrolysis process has different advantages and disadvantages so that it is difficult to

further improve the quality of pyrolysis products. To reduce the cost and improve the quality of pyrolysis products, some researchers have coupled multiple pyrolysis technologies for waste tire processing together and optimized the pyrolysis process. The feasibility and economic benefit of waste tire pyrolysis technology depend on the comprehensive utilization of the end-use of the pyrolysis products. The pyrolysis oil and gas product of waste tire pyrolysis could be used as fuel due to their high calorific value with some restrictions mainly associated with their composition of, for example, sulfur content. Moreover, pyrolysis oil can be co-fed and upgraded in existing petroleum refinery units through fluid catalytic cracking and hydrocracking to meet the

Table 3
The effect of catalysts on waste tire pyrolysis.

Catalysts	Zeolite				Al ₂ O ₃	Ca(OH) ₂	Oyster shells +			CaCO ₃	Al ₂ O ₃	MgO	Tire tread char	Side wall char
Catalysts	HZSM-5	HY	zeolite	H-SDUSY			CaCO ₃	Al ₂ O ₃	MgO					
Reactor	Conical Bed		Fixed bed				Fixed bed			Fixed bed			Fixed bed	Fixed bed
Tire size (mm)	-		2-3.5				2-3			2-3			2	2
Feeding speed	2 g·min ⁻¹		-				-			-			-	-
Catalysts to tire ratio	0.66-	1.66-	0.1				0.03			0.03			0-1.0	0.35
Pressure (MPa)	ambient pressure		ambient pressure				ambient pressure			ambient pressure			ambient pressure	0.1-2.0
Temperature (°C)	425-500		450				550			550			600	600
Heating rate (°C·min ⁻¹)	-		10				1-5			8-10			30	30
Residence time	20 ms		75 min				55-65 min			55-65 min			60	60
Catalysts Dosage (g)	15-	15	100				-			-			0-3.5	0-1.4
Addition method	Separate		separate				separate			cover/separate			separate	separate
Advantages	High activity and selectivity of zeolite owing to its high specific surface area.		High activity and selectivity of zeolite owing to its high specific surface area.		High activity and selectivity, high gas yield. Catalysts recycled easily.	High char yield and oil-gas quality. Catalysts recycled easily.	High oil gas conversion rate, high quality of oil and gas. Catalysts recycled easily.			High oil gas conversion rate, high quality of oil and gas. Catalysts recycled easily.			High activity and selectivity, high oil gas conversion. Catalysts could be recycled and used directly.	
Disadvantages	Zeolite is easily poisoned and has a short life due to high carbon deposits yield.		Zeolite is easy poisoned and has a short life. Char yield increased.		Zeolite is easy poisoned and has a short life. Char yield decreased.	Low oil gas conversion rate.	Char yield decreased.			Char yield decreased.			High carbon deposit yield.	
Carbon deposits (wt.%)	2.1-	7.9-	-	-	-	-	-	-	-	-	-	-	0-19.11	0-8.57
Oil (wt.%)	28.83-	42.92-	22.0	20.0	32.0	26.0	24.32	33.83	31.48	39.42/	32.23/	42.29/	18.57-	35.09-
Gas (wt.%)	14.90	32.25	24.6	37.4	34.1	18.4	29.91	27.30	28.09	22.55	26.26	38.43	63.71	54.32
Char (wt.%)	7.60-	3.42-	24.6	37.4	34.1	18.4	29.91	27.30	28.09	30.13/	30.13/	16.73/	2.41-	4.16-
Ultimate analysis of tire char (air dry basis)	19.38	2.57	24.6	37.4	34.1	18.4	29.91	27.30	28.09	36.94	32.93	20.03	25.26	20.02
C (wt.%)	34.15-	34.54-	53.4	42.6	33.9	55.6	43.67	37.22	36.38	37.17/	37.84/	40.45/	33.3	34.47-
H (wt.%)	34.95	35.49	53.4	42.6	33.9	55.6	43.67	37.22	36.38	40.36	40.95	41.25	33.3	42.43
N (wt.%)	-	-	-	-	-	-	79.49	87.04	86.17	83.45/	87.00/	86.12/	-	88.21-
S (wt.%)	-	-	-	-	-	-	82.74	84.17	85.21	82.74	84.17	85.21	-	88.83
O (wt.%)	-	-	-	-	-	-	1.16	1.14	1.29	1.21/	1.20/	1.27/	-	-
Proximate analysis of tire char (air dry basis)	-	-	-	-	-	-	0.31	0.27	0.29	1.22	1.23	1.34	-	-
Ash (wt.%)	-	-	-	-	-	-	0.32/	0.27/	0.29/	0.32/	0.27/	0.29/	-	-
M (wt.%)	-	-	-	-	-	-	0.25	0.22	0.31	0.25	0.22	0.31	-	-
FC (wt.%)	-	-	-	-	-	-	2.17	2.59	2.53	2.21/	2.35/	2.43/	-	1.04-
V (wt.%)	-	-	-	-	-	-	5.55	0.8	2.4	2.00	2.63	2.68	-	1.73
S _{BET} (m ² ·g ⁻¹)	-	-	-	-	-	-	5.50/	0.8	2.4	5.50/	3.88/	3.25/	-	9.28-
HHV (MJ·kg ⁻¹)	-	-	-	-	-	-	5.59	4.49	3.55	5.59	4.49	3.55	-	10.37
Refs.	[159]	[159]	[250]	[250]	[250]	[250]	[82]	[82]	[82]	[243]	[243]	[243]	[24]	[191]

- not described in the reference text.

strict requirements of commercial fuels [253]. The tire char has some characteristics such as small particle size, uniform size distribution, and small specific surface area, which suggest that it could be used as a rubber reinforcing agent, carrier of catalysts, and as an adsorbent [254]. The yield of tire char is 30-37 wt. % of the initial material and is one of the main product of waste tire pyrolysis. The utilization of tire char

largely determines the feasibility and economics of the waste tire pyrolysis process. Thus, the economy of the waste tire pyrolysis and recovery process is significantly influenced by the quality of tire char and market application demand. Therefore, in the development of processes for the pyrolysis of waste tires, it is necessary to consider the market application demand and develop a technology to rapidly improve the

Table 4
Comparison of advantage and disadvantage of waste tire pyrolysis strategies

Pyrolysis process	Vacuum pyrolysis	Pressurized pyrolysis	Microwave pyrolysis	Plasma pyrolysis	Hydro-pyrolysis	Co-pyrolysis	Catalytic pyrolysis
Reaction mechanism	The vacuum pyrolysis is to generate negative pressure, peel volatiles off solid wastes in time, and reduce the residence time of volatiles in the pyrolysis reactor.	The pressurized pyrolysis inhibits the diffusion movement of volatiles, increases the residence time of the volatile and the probability of secondary cracking reactions.	The microwave is a process whereby materials absorb the microwave heat energy and convert it into heat energy, this results in the pyrolysis of waste tires.	Electric current passes through the gas to produce a continuous arc and promotes the secondary cracking of volatiles.	Hydro-pyrolysis has the effect of regulating pyrolysis volatiles to generate more saturated volatiles.	Two materials of different compositions can complement each other advantages, have a synergistic effect, and improve the quality of pyrolysis products.	Catalysts are conducive to reducing the activation energy of pyrolysis and promoting the rapid pyrolysis of the waste tire.
Advantages	Lower pyrolysis temperature and less organic matter on the surface of char. Reducing secondary cracking, increasing oil yield.	Increased the yield of oil and char.	Heating up quickly and uniform heating; Reduced particles in the oil. Automatic thermal stabilization to avoid overheating.	Increase the yield of pyrolysis gas and quality of pyrolysis oil.	Reduce secondary re-condensation, polymerization, and energy consumption.	The quality of pyrolysis oil is improved. This technology could make up for the high energy consumption of waste tire pyrolysis.	Increase the yield of target product, decrease the activation energy, short the reaction time and reduce energy consumption.
Disadvantages	Heat transfer mode of pyrolysis furnace is external heat transfer type, low heat transfer efficiency, need to increase heat.	Tire char has melting phenomenon. High requirements for pyrolysis equipment.	Pyrolysis products are greatly affected by the pyrolysis reactor	High-voltage discharge is dangerous and needs to be prevented from exploding. High operating costs.	Hydrogen pressure has great influence on the products distribution. Expensive and complex	Pyrolysis products are affected by the heating rate and the ash content in tire char is high.	Large amount of catalyst required, catalyst sintering, high content of ash in tire char. Difficult to scale up.
Tire size	0.63-20 mm	2 mm	0.425 mm - 3 cm	0.18-0.30 mm	0.5-2 mm	0.68-1.5 cm	6-10 mm
Temperature (°C)	425-500	600	450	370-450	430	400-700	425-600
Microwave power (kw)	-	-	1.5-6	-	-	-	-
Heating rate (°C.min ⁻¹)	-	30	2.5	-	5-80	-	1-40
Power input (KVA)	-	-	-	26.4-62.5	-	-	-
Pressure (MPa)	0.025 - 0.1	0.1-2.0	Ambient pressure	Ambient pressure	Ambient pressure	Ambient pressure	Ambient pressure
N2 (mL.min ⁻¹)	3.0-9.5 L.min ⁻¹	60	-	80	-	-	30- 00
Residence time (min)	-	-	14-100 min	-	-	-	20 ms - 75 min
Dosage	3 g.min ⁻¹	4 g	60-1500	20-100 g/min	3-20 g	200 g	1-4 g
Oil (wt.%)	32.9-48.8	52.02-56.45	20.7-47.6	-	-	20-25	14.90-63.71
Gas (wt.%)	1.75-21.8	2.17-5.11	9.0-27.4	30.98-77.0	-	39-46	2.57-50.1
Char (wt.%)	34.8-51.7	32.51-35.89	36.5-65.0	21.6-69.02	33.83	30-35	34.15-53.4
Ultimate analysis of tire char (air dry basis)							
C (wt.%)	-	88.65-88.63	82.31-92.03	80-85.06	-	84.5-87.1	82.74-87.00
H (wt.%)	-	-	0.32-3.21	0.24-0.42	-	10.1-10.2	1.20-1.34
N (wt.%)	-	-	0-0.78	0.38-0.42	-	0.6-0.7	0.22-0.32
S (wt.%)	-	1.04-1.73	1.3-2.3	1.97-2.70	-	0.6-0.9	2.00-2.68
O (wt.%)	-	9.28-10.12	6.45-7.87	12.35-13.9	-	1.1-4.2	3.25-5.59
Proximate analysis of tire char (air dry basis)							
Ash (wt.%)	-	-	5.88-9.50	15.14-16.25	12	-	5.26-8.17
M (wt.%)	-	-	-	-	-	-	-
FC (wt.%)	-	-	76.23-89.30	-	-	-	-
V (wt.%)	-	-	1.77-17.90	-	-	-	-
S _{BET} (m ² .g ⁻¹)	90.0	58.02-64.33	-	61-70	50-70	-	-
HHV (MJ.kg ⁻¹)	-	-	30-36	28.5-28.7	-	41.3	9.16-16.18
Refs.	[156,184,188]	[191]	[197,202, 204]	[209,210]	[214,216]	[226,228,229,236, 255]	[159,243,244,247, 250,256,257]

-Not described in the reference text.

quality and value of tire char.

3.3. Pyrolysis process conditions

Pyrolysis process conditions are an indispensable influencing factor in the pyrolysis of the waste tires. Generally speaking, the general pyrolysis conditions include tire particle size, pyrolysis temperature, heating rate, pressure, and the presence of a catalyst. These conditions greatly affect the tire degradation reaction mechanism, therefore the

yields and composition of pyrolysis products.

3.3.1. Particle size

With the increase in waste tire production, how to process the waste tire quickly and obtain higher value is the main goal pursued at present. To industrialize and commercialize the pyrolysis of waste tires, the particle size of the waste tire was often ignored in most earlier studies. Therefore, in these early preliminary studies often performed in laboratory-scale units, the significant effect of heat and mass transfer

limitations associated with tire particle size was not considered. The particle size of tires affects the rate of heat transfer and heat absorption, thereby affecting the rate of tire pyrolysis. It is worth noting that the influence of the tire particle size requirement strongly depends on the technology and reactor used in the pyrolysis process. The tire particle size typically ranges from 0.5 mm in a fluidized bed reactor to the use of whole, un-shredded tires in a fixed bed. The particle size is important for fast pyrolysis using a fluidized bed reactor where it is essential to maintain fluidization, whereas using slow pyrolysis processing with a fixed bed reactor; even, a whole tire can be pyrolyzed via batch treatment. The increase in particle size from 75 μm to 850 μm has been reported to lead to a significant increase in the temperature gradient range inside the particle [258]. Moreover, the larger the particle size, the lower the tire particle effective heating rate. Accordingly, the pyrolysis reaction takes place at a lower temperature and the reaction rate is reduced [259,260]. Particle size (165 μm – 1000 μm) has also been reported as an important influencing factor in the yield of the waste tire pyrolysis products and their characteristics [261]. The waste tire with a small particle size will generate more yield of pyrolysis oil and less yield of tire char. The smaller particle size helps to increase a convective energy flow in the sample and to accelerate the particle degradation [262]. The yield of tire char showed an increase with particle size increase, which was also reported elsewhere in the literature [85,100,263]. The particle size of the waste tire in the pyrolysis process determines the magnitude of the overall energy used and the completion time of the pyrolysis reaction [260]. Mui et al. [264] reported that tire char yield increased from 35.15 to 37.15 wt. % with the particle size of tire feedstock increasing from 0.5 to 2.0 mm. Also, the carbon content (88.88 wt. %) in the tire char obtained from the smaller particle size feedstock was higher than that (81.24 wt. %) obtained from the larger particle size, while the sulfur (1.67 wt. %) and ash (8.93 wt. %) content in tire char obtained from the large particle size were higher than those (sulfur content 1.40 wt. % and ash content 7.84 wt. %) obtained from the smaller particle size. Also, the specific surface area of tire char increased from 117 $\text{m}^2\cdot\text{g}^{-1}$ to 156 $\text{m}^2\cdot\text{g}^{-1}$ with the feedstock particle size increase. This phenomenon was also reported in other papers [86,265], where the tire char yield reached 37.8 wt. % with a large particle size feedstock (3 cm \times 1.5 cm) [265]. The carbon content in tire char could reach 95.9 wt. %, sulfur content reached 2.3 wt. %, and ash content was 2.6 wt. %. The specific surface area was low at only 65 $\text{m}^2\cdot\text{g}^{-1}$. Tanet et al. [98] studied the effect of pyrolysis conditions on the yield of pyrolysis products from the pyrolysis of waste tires. The yield of tire char increased with the increase of particle size (0.5–15 mm). It should be finally noted that the grinding of waste tires to reduce the particle size is an energy-intensive process, moreover, energy requirement grows exponentially with waste tire size reduction [266].

It should be also noted that the original tire particle size determines that of the produced char. Char particle size has a great impact on the porosity development throughout the activation process as long as the process is controlled by pore diffusion and the accessibility of the activation agent, commonly steam and carbon dioxide. In large char particles, efficient diffusion is hindered provoking non-homogeneous gasification and therefore activated carbon is highly mesoporous with poor microporous development [40]. Overall, it is clear that the particle size of the waste tire feedstock affects the tire char yield and components, accordingly, the particle size of the tire should be carefully assessed in the tire pyrolysis process development.

3.3.2. Tire type

The pyrolysis products vary in terms of field and chemical composition depending on the source of the tires. Tire type and brand affect the tire char yield and quality due to the different components used in the manufacture of the tire and consequently the pyrolysis behavior of components and how they affect the tire rubber degradation process during pyrolysis will be different. The pyrolysis products obtained from two different tire types (passenger car tires and truck tires) was reported

[51]. Under the same pyrolysis condition, the yield of tire char obtained from passenger car tires reached 42.0 ± 2.5 wt. %, while, truck tire char yield reached 33.8 ± 2.8 wt. % at 550 °C pyrolysis temperature. The carbon contents in passenger car tires and truck tires were 74.30 and 83.20 wt. %, respectively and the ash contents were 18.9 and 5.0 wt. %, respectively. The higher ash content in the passenger car tire resulting in a higher tire char yield. Rohit et al. [52] reported the pyrolysis product distribution of three different tire types, LVT (motorcycle tires, bicycle tires), MVT (car tires), and HVT (bus tires, lorry tires). The ash contents in LVT, MVT, and HVT are 7.4, 15.32, and 5.67 wt. %, respectively. The carbon contents in LVT, MVT, and HVT ranged very little, from 84.2 wt. % in LVT to 89.5 wt. % in HVT. The tire char yields of LVT, MVT, and HVT were approximately 38.0, 43.0, and 33.0 wt. % at 700 °C, respectively. High ash content in MVT resulted in high tire char yield. However, it was reported that the yields of tire char from HVT are lower than those from LVT and MVT [49]. The tire char yields obtained from different brands of tire are different [50], which were reported to be 37.5 (Debica brand), 38.1 (Dunlop brand), 37.1 (Goodyear brand), 38.0 (Courier brand), 41.7 (Michelin brand), and 38.3 wt. % (Continental brand), respectively. The ash contents in these six brands of tires were reported as 2.66, 4.81, 4.98, 3.39, 2.39, and 6.23 wt. %, respectively. The tire char yields obtained from the different parts of the waste tire are also variable due to the different components used in the manufacture of the tire. For example, the ash content in the tire tread was reported as 18.04 wt. %, while in the tire side wall it was only 2.14 wt. % [69]. This will also influence the production and characteristics of the product tire char, for example, the specific surface area of tire tread char (121.47 $\text{m}^2\cdot\text{g}^{-1}$) is higher than that of side wall char (44.72 $\text{m}^2\cdot\text{g}^{-1}$). The high ash content in the tire tread resulted in a higher tire char yield of the tire tread than that of the side wall, and low carbon content in the tire tread char. The shortcoming of these studies is that they have not carried out further research on the characteristics of the product tire char.

3.3.3. Temperature

Pyrolysis temperature plays a vital role in whatever the pyrolysis process is used and the derived pyrolysis product yields and their composition. The temperature determines the amount of energy input and affects the degree of molecular bonds breakage. It has been reported that the tire char yield dropped from 86 to 41 wt. % when the pyrolysis temperature was increased from 300 to 500 °C, and then remained constant at higher temperatures [261]. The lower pyrolysis temperature indicating incomplete pyrolysis and a consequent increase in the solid residue. Thus, 500 °C is usually regarded as the optimum pyrolysis temperature as long as it is the minimum temperature to ensure complete rubber devolatilization and at the same time attenuate secondary reactions. The pyrolysis temperature for maximum oil production has been usually reported for waste tire pyrolysis for several different reactor designs at approximately 500 °C [72,84,97]. The influence of pyrolysis temperature could be divided into initial temperature, final temperature, and heating rate [267]. The pyrolysis temperature mainly affects the pyrolysis time and the yield of pyrolysis products. (i) Within a certain temperature range, the increased temperature gives a higher pyrolysis rate and a shorter pyrolysis time. (ii) When the temperature is less than 500 °C, the pores of the tire char are not expanded, resulting in incomplete pyrolysis of the waste tire, high yield of tire char, and poor quality of char due to the surface adhesion of pyrolysis volatiles [114,268]. When the pyrolysis temperature is higher than 500 °C, the partial pores of the tire char are expanded, and thereby the specific surface area of the char is increased. However, at high temperatures, tire char is easy to be sintered, resulting in the blockage of char pores, the reduction of micropore/mesoporous volume, the reduction of specific surface area, and poor surface properties [237]. With the increase of pyrolysis temperature and heating rate, the pyrolysis time is shortened, the yield of char decreased, and finally reaches a stable value [269]. The influence of temperature on pyrolysis products was studied [270] and showed that when the temperature was increased from 500 to 700 °C, the increase in

temperature resulted in a decrease in the yield of char. The tire char contains O, Si, Na, Al, Ca, Zn, and other elements, and with a temperature higher than 700 °C there is the potential for loss of volatile additives such as zinc and sulfur [271]. It should be noted that the increase in temperature is usually associated with higher ash and sulfur contents in the produced char, this effect is related to the lower char yield obtained and the concentration of the ash metals in the char, moreover, it can be attributed to the reaction between sulfur and zinc oxide (added in tire vulcanization), producing ZnS [32,76,272,273]. However, a further increase in temperature above 650 °C showed no increase in the tire char ash content [274,275], these results may be associated with the removal of an organometallic component like Zn at high temperature [275].

With the increase in temperature, the specific surface area of char firstly increased and then decreased [264]. The total pore volume and specific surface area showed the same trend, with fewer microporous structures and resulting in mainly a char consisting of mesoporous structures. Low temperature leads to incomplete pyrolysis of the waste tire, resulting in a higher content of phenols, alcohols, and other substances attached to the char surface than that of high-temperature tire char, therefore the content of hydrogen and sulfur in tire char obtained at low pyrolysis temperature was higher than that obtained from high temperature [264]. This phenomenon of sulfur distribution in tire char was also confirmed in the reports by Wang et al. [269].

Moreover, pyrolysis temperature significantly affects char reactivity which is of special relevance for its upgrading to activated carbons. Thus, Zabaniotou et al. [276] analyzed the air reactivity of tire chars obtained from tire pyrolysis over the temperature range of 390 to 860 °C. The increase in pyrolysis temperature improved char reactivity for chars produced at temperature of up to ~600–650 °C, however, reactivity gradually decreased at higher pyrolysis temperatures. The reduction of char reactivity at high temperatures may be associated with thermal annealing [277]. In fact, at pyrolysis temperatures of about 800 °C, the char structure gradually becomes more ordered, and consequently more refractory and less reactive.

3.3.4. Heating rate

The heating rate of the tire during the pyrolysis process has an effect on the yield and characteristics of the product tire char. In fact, the heating rate is a key variable in waste tire pyrolysis as long as it determines pyrolysis temperature. The heating rate affects the rate of heat transfer, the effective actual temperature, and the pyrolysis thermal degradation of the tire. Thus, the higher the heating rate, the higher the effective pyrolysis temperature [137,267]. Depending on the pyrolysis technology and reactor used, different situations can occur: (i) slow and controlled heating rate conditions when using batch reactors, mainly fixed beds [1,112]; (ii) non-controlled very fast heating rates typical of fast pyrolysis technologies, i.e., fluidized beds, spouted beds or ablative reactors [96,100,155,278]; (iii) intermediate heating rates such as those of microwave reactors or rotary kilns [94,203,204]. As waste tires processed to a suitable particle size are directly fed into a fluidized bed reactor, the tire particles are heated with a very high heating rate. Since it is very difficult to measure the heating rate of particles directly, few researchers obtained the information through the way of process calculating.

The kinetics and heat flow modelling of waste tires at different heating rates was studied [280] and it was reported that during the pyrolysis process of the tire, the reaction performance of the first endothermic peak is independent of the heating rate. Because the magnitude of the heat of vaporization is much higher than that of the exothermic reaction heat, the thermal absorption performance of pyrolysis is stronger at a higher heating rate. It was also found that more uncondensed gas was produced and the average molecular weight of pyrolysis oil decreases. At the same time, the tire char yield decreased with the increase in heating rate at the same temperature in a fixed bed batch reactor. When the temperature was at 600 °C, the tire char yield decreased from 40.2 wt. % to 32.8 wt. % with a heating rate increase

from 5 °C min⁻¹ to 80 °C min⁻¹. These results also have been investigated in the earlier literature [137]. The yield of tire char under a fast heating rate (110 °C min⁻¹) was higher than that under a slow heating rate (10 °C min⁻¹) [98]. Fig. 14 shows the TG and DTG curves at different heating rates for waste tires for experiments undertaken using thermogravimetric analysis. The increase in heating rate results in the weight loss thermogram move towards the high-temperature region. When the temperature is higher than 550 °C, the waste tire pyrolysis is complete. The heating rate has an effect on the yield of tire char. When the temperature is lower than 550 °C, the char yield is increased with the increase in heating rate [36,279]. These TG analyses showed that the heating rate had an influence on the yield of tire char under low temperature but also at high temperature. The heating rate of TG experiments provided little value since the heating rate is usually relatively slow in TG experiments, however, TG analyses provides a basic theoretical mechanism for the effect of heating rate on tire char yield.

The effect of heating rate in the range of 1 to 20 °C·min⁻¹ for tire pyrolysis using a fixed bed reactor was studied [264], and it was shown that the increase in heating rate reduced the char yield from 38.7 to 36.8%. This decreasing trend of tire char yield is in good agreement with those observed by Wang et al. [269] pyrolyzing tires with fixed beds under much higher heating rates, in the 60 to 6000 °C·min⁻¹ range, and operating with final temperatures between 425 and 575 °C. At the same final pyrolysis temperature, the tire char yield decreased as the heating rate was increased. When the temperature was at 575 °C, the tire char yield decreased from 43 wt. % to 41 wt. % with the heating rate increasing from 60 °C min⁻¹ to 6000 °C min⁻¹. The higher yield at the lower heating rates can be attributed to the homogeneous and slow heating of tire particles, which increases the time for secondary reactions of polymerization and condensation to occur between degradation intermediates involved in the formation of carbon deposits on char particles [99,267,281].

The heating rate not only plays a significant role in char yield but also in the char characteristics. In this respect, Williams et al. [137] reported a positive effect of the heating rate increase on the features of tire derived char. The authors investigated tire pyrolysis in a fixed bed reactor operated at different final temperatures of, 300, 420, 600, and 720 °C, and with heating rates between 5 and 80 °C·min⁻¹. Thus, at all the pyrolysis temperatures the increase in heating rate improved the surface area of the produced chars given that tire particle fast heating promotes rubber devolatilization and attenuates pore blockage by the formation of carbonaceous deposits. Mui et al [264], reported that the BET surface area of product tire char was improved with the increase in tire pyrolysis heating rate from 1 to 5 °C·min⁻¹ however, a further increase of heating rate showed a negative effect. However, in another report, the char yield decreased when the heating rate was increased [269]. The sulfur distribution in tire char decreased with the heating rate increasing at the same temperature, and more than half of the sulfur existed in the tire char.

3.3.5. Pressure

The pressure involved in the pyrolysis process plays a role in the yield and quality of pyrolysis products and also affects the movement behavior of volatiles. Increasing the pressure prevents the removal of volatiles from the raw materials and increases the residence time of volatiles in the reactor. The pyrolysis volatiles could be cracked into smaller organic compounds under the conditions of increasing pressure. It has been reported that with the decrease of pressure, the residence time of pyrolysis volatiles on the surface and within the pores of the solid phase was shortened, resulting in a high yield of pyrolysis oil and gas but a low yield of tire char [191]. Under vacuum conditions, the volatiles matter is promoted to release from the surface of the waste tire, this resulted in the pyrolysis volatiles of waste tires remaining for only a short time in the reactor, which helped to reduce the secondary cracking reactions of the volatile phase in the pyrolysis reactor [156,181]. Moreover, the operation under vacuum conditions and the subsequent

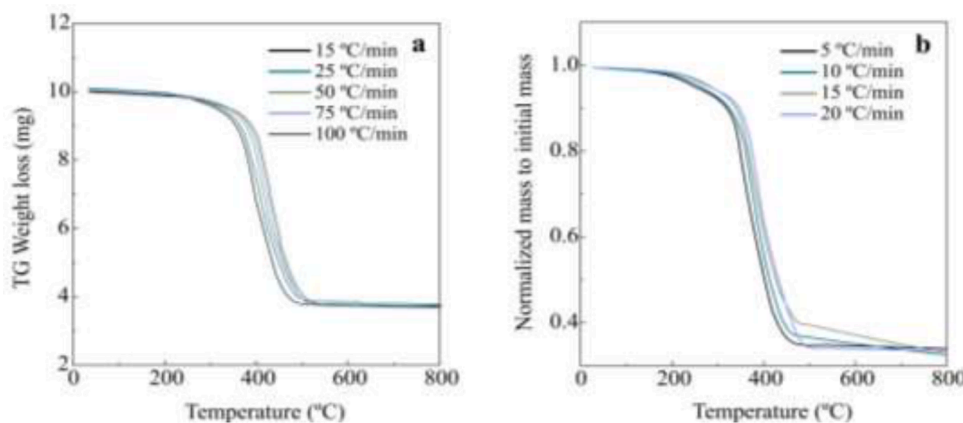


Fig. 14. The TG thermograms of waste tire at different heating rate, (a) [279] and (b) [36].

pressure gradient promotes the diffusion of pyrolysis volatiles formed inside the tire particle towards the outside, reducing the impact of secondary reactions [156]. In addition, this effect also improves the tire degradation rate and eases tire conversion [282]. The carbon deposition on the surface of char obtained from the waste tire under vacuum conditions has been reported to be low [184], accordingly, the surface area of the resultant char was improved [156]. According to Roy et al. [187], vacuum conditions should be combined with high pyrolysis temperatures to minimize hydrocarbon adsorption on the carbon black surface and the subsequent formation of carbonaceous deposits. Accordingly, char properties similar to those of the original virgin carbon black added during the tire formulation process can be obtained. Under vacuum conditions, the char yield was 34.8 wt. % at 600 °C [93] and lower than that 35.89 wt. % at 600 °C under 2.0 MPa. Under vacuum conditions, it is conducive to the gas yield rather than tire char yield. Under atmospheric pressure, the residence time of pyrolysis volatiles in the reactor was longer, which increased the secondary reactions of these volatiles. The pyrolysis oil attached to the surface of tire char blocked the pores of the char, resulting in a high yield, but the char was of poor quality, with a low specific surface area. The change of pressure not only affects the yield of char but also affects the specific surface area and pore diameter distribution of tire char [191]. With the increase of pressure (0.1–2.0 MPa), the yield of tire char increased from 32.51 to 35.89 wt. % at 600 °C, and the specific surface area of tire char decreased from 64.33 to 58.06 m²·g⁻¹. The product tire char from the pressurized pyrolysis process had a distinct catalytic role in the cracking of volatiles.

3.3.6. Residence time

Residence time directly affects the secondary reactions of pyrolysis volatiles attached to the surface and within the pores of the tire char and the pyrolysis degree of the waste tire. Residence time includes two aspects: one is the residence time of pyrolysis volatiles; another is the residence time of feedstock in the reactor. The carrier gas flow rate is inversely proportional to the residence time, that is, the higher the carrier gas flow rate, the shorter the residence time. In the pyrolysis process, the carrier gas is often required to facilitate the volatiles to leave the pyrolysis reactor thereby separating the gases from the raw tire to achieve the purpose of obtaining pyrolysis oil, gas, and char. Carrier gas mainly affects the yield and quality of pyrolysis products through flow rate and gas type [21]. Some research workers studied the influence of residence time on the yield and quality of pyrolysis products by manipulating the carrier gas flow rate [283,284]. The yield of tire char under long residence time was significantly higher than that under short residence time [98]. In addition, the increase in residence time also promotes secondary cracking reactions with the subsequent reduction in oil yield [100,112]. Moreover, carrier gas type also affects the pyrolysis products derived from waste tires. Compared with nitrogen as carrier gas used in the waste tire pyrolysis process [285], the use of recycled

pyrolysis gas and steam as carrier gas both were beneficial to increase the yield of tire char. The yield of tire char obtained in a CO₂ atmosphere was lower than that in an N₂ atmosphere [286]. When the temperature is higher than 800 °C, the yield of tire char will continue to decline under a CO₂ atmosphere due to its partial gasification by the CO₂. This phenomenon has been reported in the literature [5,287]. The yield of char obtained from a mixture of different carrier gases (CO₂, CO₂ + steam) was lower than that where only an argon atmosphere was used [98].

To ensure complete waste tire pyrolysis and completely remove volatiles, the residence time of the tire in the pyrolysis reactor should be extended as far as possible. But, the yield of tire char obtained with long residence times was less than that in short residence times. This has been investigated by Edward et al. [264] and showed that the tire char yield decreased with the increase of the residence time of the feedstock in the reactor (1–4 h). The longer the residence time of feedstock, the carbon content in tire char was reduced, and the ash and sulfur content of the tire char was higher. The pyrolysis of waste tires is an endothermic process and is relatively slow. When the absorbed energy reaches the required energy for waste tire pyrolysis, the waste tire could be completely pyrolyzed. The heat energy absorbed in a short time cannot satisfy the energy for the complete cracking of the waste tire, and this short residence time results in a higher yield of tire char generated in the pyrolysis of waste tires. The more energy that is absorbed over a long time, leads to complete cracking of the tire rubber and the generation of a low yield of tire char. The residence time of the waste tire in the reactor clearly affects the yield of tire char. The effect of the residence time of feedstock is particularly obvious in moving bed reactors, such as rotary kiln reactors and fluidized beds. If the residence time is too short, no matter how high the pyrolysis temperature, the waste tire could not be decomposed completely, and resulted in a high yield and poor quality of tire char. If the residence time is long and the temperature is too low, the waste tire also could not be completely decomposed, and this resulted again in high yield and poor quality of tire char. It has been reported that the tire char yield was 33 wt. % at 500 °C where the residence time of the tire was 30 min using a moving bed reactor [99], and the sulfur content in tire char was 3.8%. However, the tire char yield could reach 45 wt. % at a pyrolysis temperature of 500 °C maintained for tire pyrolysed for 20 min with a fixed bed reactor, and produced a char with a specific surface area of only 50.03 m²·g⁻¹, and with a sulfur content in tire char of 1.31% [288]. In another study, the tire char yield was 41.2 wt. % when the waste tire residence time was 15 min at 850 °C with a rotary kiln reactor, while the specific surface area of the tire char was only 40 m²·g⁻¹, with a sulfur content of 3.0% [169]. These differences in the yield and characteristics of the tire char are mainly because the residence time was different, but also other reasons are the reactor configuration and the feed mode of the waste tires. The high temperature was suitable for removing volatiles and produced a lower yield of tire char, but, a certain improvement in tire char quality, especially its BET surface area [155,

180,289], resulted in a high cost to the waste tire pyrolysis process.

It can be observed from Table 5 that the pyrolysis process has an important influence on the quality of the products from pyrolysis of waste tires. The mechanism of different pyrolysis conditions is different. Tire type as the source of tires for the pyrolysis process affects the quality of waste tire pyrolysis products in the pyrolysis process due to different components within the tire. Particle size and heating rate affect the rate of heat transfer in waste tire pyrolysis and the final temperature and residence time determine the degree of tire pyrolysis. To obtain a high-quality tire char, the pyrolysis process needs to be considered comprehensively.

To sum up from Sections 3.1 to 3.3, the yield and quality of tire char are influenced by various factors. The source of tire rubber is the original influential factor in relation to pyrolysis product distribution because its composition can vary considerably depending on the requirements of the tire use. The pyrolysis conditions, technology and equipment used

are factors in the treatment process in the waste tire pyrolysis step. To acquire the target product, these influencing factors should be comprehensively considered.

4. Tire char characteristics

The physical and chemical characteristics of the waste tire char have been reported in many research articles [21,148,155,290,291]. It is of great interest to understand the structural characteristics of tire char for its further application. The modification scheme of tire char could be determined by its structural characteristics.

4.1. Physical structure characteristics

The physical characteristics of tire char mainly include pore diameter, pore volume, specific surface area, and composition. The common

Table 5
The effect of pyrolysis process conditions on products quality.

Process condition	Particle size	Tire type							Temperature	Heating rate	Pressure	Residence time	
Mechanism of action	The particle size of tires affects the rate of heat transfer and heat absorption, thereby affecting the rate of tire pyrolysis.	The components of different types of tires are different, and the pyrolysis behavior of components is different.							The temperature determines the amount of energy and affects the degree of molecular bonds breakage.	The heating rate affects the rate of heat transfer, the effective actual temperature, and the pyrolysis degradation of the tire.	The pressure affects the movement behavior of volatiles. Increasing the pressure prevents the leave of volatiles from the raw materials and increase the residence time of volatiles in the reactor.	The residence time affects the secondary reaction of tire volatiles and the pyrolysis degree of the tire.	
Tire type	-	PCT	TT	LVT	MVT	HVT	TTR	SWR	-	-	-	SWR	-
Temperature (°C)	500	550					500		400-900	500	450-600	600	500
Particle size (mm)	0.5-2.0, 3 × 1.5 cm	1.5-2.0 mm	1-3 cm				3 × 2.0 cm		1.0-2.0, 3 × 1.5 cm	1.0-2.0	0.2-0.8 mm	2 mm	1.0-2.0
Heating rate (°C.min ⁻¹)	5	7	20				10		5	1.0-20.0, 60-6000	20	30	5
Pressure (MPa)	Ambient pressure	Ambient pressure							Ambient pressure	Ambient pressure	0.0035-0.004	0.1-2.0	Ambient pressure
N ₂ (mL.min ⁻¹)	-	-	-				100		-	200	-	60	-
Residence time (h)	1.5-2.0	1.0	-				0.5		1.5-2.0	2.0	-	1.0	1.0-4.0
Dosage	100 g-3.0 kg	130g	200 g				12 g		100 g	100 g, 5 mg	100	4 g	100 g
Oil (wt.%)	55.93	47.4	55.6	43.10	53.51	43.18	-	-	52.72-58.17	-, 56.04-56.38	32.9-48.8	52.03-56.45	-
Gas (wt.%)	5.79	7.4	7.6	12.06	12.74	17.29	-	-	4.87-9.46	-, 0.17-1.45	15.4-21.8	22.17-5.11	-
Char (wt.%)	35.15-38.16	42.0	3.0	44.16	32.59	38.41	42.72	32.21	32.34-50.10	36.8-38.7, 42.39-43.41	51.7	32.51-35.89	35.66-38.45
Water (wt.%)	-	3.2	33.8	-	-	-	-	-	-	-	-	-	-
Proximate analysis of tire char (air dry basis)													
M (wt.%)	0.4	-	-	-	-	-	3.05	1.02	0.3-0.5	-	-	-	-
V (wt.%)	2.8	-	-	-	-	-	4.83	4.89	2.3-3.0	-	-	-	-
Ash (wt.%)	7.84-11.9	40.3	14.3	-	-	-	46.54	6.54	7.25-12.96	-	13.25	-	8.86-9.24
FC (wt.%)	-	56.3	82.4	-	-	-	45.58	87.55	-	-	85.18	-	-
Ultimate analysis of tire char (air dry basis)													
C (wt.%)	81.24-90.6	-	-	-	-	-	50.65	88.81	80.26-95.9	-	85.18	-	76.50-82.39
H (wt.%)	0.20-1.58	-	-	-	-	-	0.40	0.57	0.99-2.12	-	1.15	-	1.16-1.58
N (wt.%)	0.24-0.7	-	-	-	-	-	0.47	0.48	0.20-1.1	-	0.639	-	0.20-0.24
S (wt.%)	1.40-2.3	0.8	2.1	-	-	-	-	-	1.67-2.62	-	2.03	-	1.67-2.29
O (wt.%)	1.19-6.34	-	-	-	-	-	-	-	0.07-7.66	-	-	-	5.68-10.36
S _{BET} (m ² .g ⁻¹)	117-156	55.5	56.5	-	-	-	121.47	44.72	10-156	94-156	67.96	58.06-64.33	86-156
HHV (MJ.kg ⁻¹)	-	14.8	33.9	-	-	-	-	-	-	-	-	-	-
Refs.	[264,265]	[51]	[52]				[69]		[264,265]	[264,269]	[93]	[191]	[264]

- not described in the reference text.

PCT- passenger car tire, TT- truck tire, TTR-tire tread rubber, SWR-side wall rubber.

detection techniques of physical characteristics include elemental analysis, proximate analysis, SEM, EDS, TGA, XRF, BET, and Raman spectroscopy [292]. Further characterization of tire char is through, element analysis, proximate analysis, the fixed carbon content, and ash content. The ash content also could be determined by TGA under an air atmosphere [293].

Tire char is a carbonaceous material with high carbon content, usually, it is higher than 85%, whose main origin is the carbon black added in the tire formulation process. Moreover, throughout the pyrolysis process, the formation of carbonaceous deposits over the tire char surface takes place, produced from the pyrolysis volatiles secondary condensation and depolymerization reactions. The extent of these reactions greatly depends on process conditions [156,187,294]. The heating value of tire char is associated with high carbon content. The HHV of tire char is reported in the literature to range between 25 and 32 MJ·kg⁻¹, [75,164,295–297]. However, the interest in tire char as a solid fuel is hindered by the high sulfur content.

The stability of tire char could be tested by analysis using TGA under an inert gas atmosphere. Compared with the tire char obtained at high temperatures, the properties of low-temperature tire char are more unstable due to the waste tire not being completely thermally degraded. This may be due to the decomposition of inorganic compounds on the surface of tire char at high temperatures [69]. The presence of disorder in carbon and graphene 2D hexagonal lattice in the tire char with Raman spectra has been reported [69]. Meanwhile, the results of elemental and proximate analysis of the char produced from pyrolysis of the side wall of the tire were totally different from those of the char produced from the pyrolysis of the tire tread. The ash content in the side wall rubber char was lower than that in the tread rubber char [24]. The specific surface area and pore diameter could be determined by N₂ adsorption-desorption (BET) analysis at -196 °C. Many reports have shown that the specific surface area of tire char was less than 140 m²·g⁻¹ [296,298], in addition, there are more mesopores and few micropores in tire char [24,69]. Table 6 shows the comparison of tire char

characteristics reported in the literature.

As Table 6 shows, the physical structure of the tire char produced from different tires is very different. It should be noted that these features strongly depend on the nature of the carbon black used in tire formulation and on pyrolysis conditions, especially, temperature, residence time, and pressure. A large difference was shown to exist in the char produced from the pyrolysis of the tire side wall rubber and the tire tread rubber.

4.2. Chemical structure characteristics

The chemical characteristics of tire char mainly include the surface functional groups and calorific value. The chemical characteristics of tire char could be determined by FT-IR, XRD, and HHV [69]. The type and strength of the surface functional groups could be clearly shown by FT-IR. Usually, the surface functional groups of tire char include phenols, alcohols, carboxylic acid [300], and C-O/C-O-C chemical structures [301]. It has been reported that higher sulfur retention on the surface of tire char was obtained at low temperature compared with that obtained at high temperature, which was due to the relatively high sulfur volatility at high temperature and some stable metallic sulfides which remain in the tire char [302]. XRD results also indicated that some graphitization appeared in the tire char, which was reflected by two main peaks at around 2θ = 24° and 45° [303]. In addition, these results were also confirmed by Raman spectra, illustrated in Fig. 15. The degree of graphitization of tire char was different for chars produced at different pyrolysis temperatures and residence times [69,304] (Fig. 15). Also, high pressure promotes high yield and graphitization of tire char [191]. The heat value of tire char is typically ~30.7 MJ·kg⁻¹ (Table 6). The surface nature of activated char from the waste tire was reported to be hydrophobic [305].

Table 6
Comparison of tire char reported in the literature.

	Side wall char-550 (ad)	Tire tread char-550 (ad)	Tire char	Tire char (ad)	Tire char	Tire char (db)	Tire char (ar)
Proximate analysis of tire char							
M (wt.%)	1.02	3.05	3.5 (ar)	1.4	3.00 (ar)	-	0.09
FC (wt.%)	87.55	45.58	79.0 (db)	62.7	81.44 (db)	85.7	90.8
V (wt.%)	4.89	4.83	4.2 (db)	25.0	3.32 (db)	1.8	0.67
Ash (wt.%)	6.54	46.54	13.3 (db)	11.0	15.24 (db)	12.5	8.41
Ultimate analysis of tire char							
C (wt.%)	88.81	50.65	82.5 (daf)	84.8	93.77	86.3	90.27
H (wt.%)	0.57	0.40	0.8 (daf)	0.5	1.04	0.3	0.26
N (wt.%)	0.48	0.47	0.0 (daf)	0.3	0.42	0.3	0.16
O* (wt.%)	-	-	12.7 (daf)	-	0.08	10.3	-
S (wt.%)	0.52	0.98	4.0 (daf)	2.9	4.70	2.8	1.22
Zn/(ZnO)	0.38(Zn)	1.47(Zn)	37.0(ZnO)	-	32.36(ZnO)	-	-
Si/(SiO ₂)	0.12(Si)	0.30(Si)	40.6(SiO ₂)	-	46.18(SiO ₂)	-	-
Al/(Al ₂ O ₃)	0.08(Al)	0.01(Al)	2.3(Al ₂ O ₃)	-	2.36(Al ₂ O ₃)	-	-
Ca/(CaO)	0.10(Ca)	0.05(Ca)	6.6(CaO)	-	7.54(CaO)	-	-
Na/(Na ₂ O)	0.05(Na)	0.22(Na)	1.2(Na ₂ O)	-	0.43(Na ₂ O)	-	-
Fe/(Fe ₂ O ₃)	0.04(Fe)	0.04(Fe)	1.4(Fe ₂ O ₃)	-	1.31(Fe ₂ O ₃)	-	-
Mg/(MgO)	-	-	1.4(MgO)	-	1.39(MgO)	-	-
S/(SO ₃)	-	-	7.5(SO ₃)	-	6.62(SO ₃)	-	-
K/(K ₂ O)	-	-	1.0(K ₂ O)	-	1.03(K ₂ O)	-	-
Ti/(TiO ₂)	-	-	-	-	0.12(TiO ₂)	-	-
Fe/(Fe ₂ O ₃)	0.04	0.04	-	-	-	-	-
S _{BET} (m ² ·g ⁻¹)	44.72	121.47	-	32.0	31.26	-	63
Micropore volume (cm ³ ·g ⁻¹)	-	-	-	-	-	-	-
Mesopore volume (cm ³ ·g ⁻¹)	-	-	-	0.0	-	-	-
V _{tot} (cm ³ ·g ⁻¹)	0.17	1.10	-	0.2	-	-	0.32
D _p (nm)	14.96	36.15	-	-	32.1	-	-
HHV(MJ·kg ⁻¹)	-	-	-	30.69	-	29.7	-
Refs.	[69]	[69]	[292]	[296]	[299]	[295]	[72]

- means not tested; * by difference; ar: As received basis; db: Dry basis; daf: Dry-and-ash-free basis

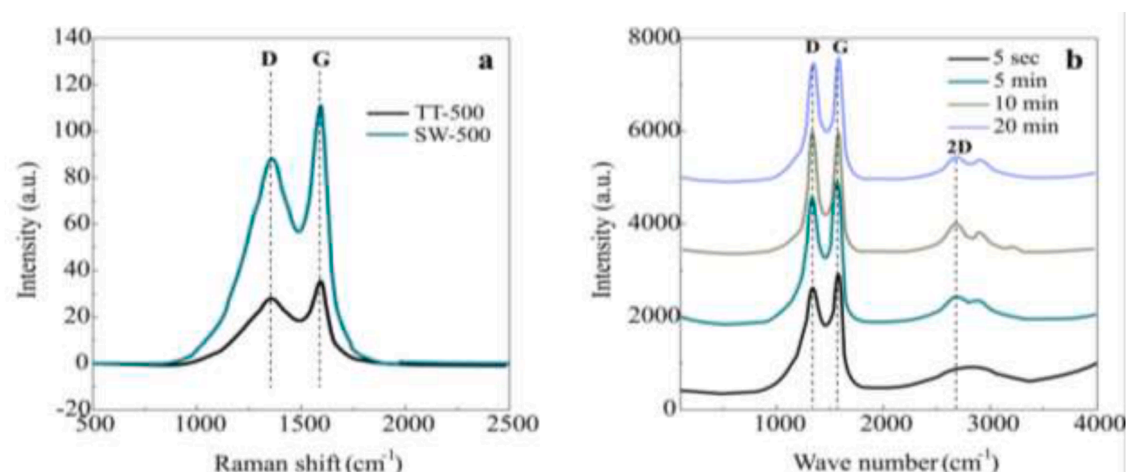


Fig. 15. Raman spectra: (a) side wall rubber char and tread rubber char obtained at 500 °C [69] and (b) rubber char at 1550 °C with different pyrolysis time [304].

5. Modification of tire char

Some researchers have reported that untreated tire char could be a substitute for commercial carbon black for rubber additives and has a potential value for recycling [155,306]. The ash content in tire char can limit the end-use application of tire char [307]. The high sulfur content of tire char also represents a major drawback for its utilization [148]. A further drawback of tire char is the potential for ash and volatile oily matter to stick to the surface of tire char during the pyrolysis process, causing pores to clog and act as agglomerating particles. Therefore, tire char is required to be modified and purified before use because its quality was shown to be poorer than that of commercial carbon black [35].

It is worthy of note that the high ash content of tire char is mainly related to the minerals added in the tire manufacturing process [278]. Different processes have been proposed for tire char demineralization and the improvement of its commercial value. For example, ash leaching can be performed prior to or after tire pyrolysis. The ashes present in the tire rubber can modify the reaction pathway and selectivity of the pyrolysis reactions. Moreover, the demineralization of the feedstock can also promote the reduction of process equipment corrosion and the formation of hazardous species during pyrolysis [308].

The main constituent of waste tires ashes is ZnO, moreover, other metallic species commonly present are Fe, Al, Ca, and Mg [291,307,309,310]. The preferred process for tire demineralization is leaching. The performance of this liquid-solid extraction process depends on several factors, especially, the properties of the feedstock (particle size or initial porosity), operating conditions (temperature, contact time, leaching rate, or agitation) the composition of the ashes and its solubility [311]. Different leaching reagents have been used in the tire or tire char demineralization, depending on the pH, solvents are classified into three groups: water, acid, and alkaline. Amongst them, acid leaching (HCl, H₂SO₄, or HNO₃) are more commonly used in previous literature reports [303,312–314]. The porous nature of tire char eases the leaching process with respect to that of the original tire rubber, in fact, the efficient ash removal only occurs on the surface of tire rubber [315].

Tire char demineralization is an especially interesting prior activation process, thus, minerals removal promotes the creation of new mesopores and micropores, where these pores then act as active sites in the subsequent activation step [33,316]. Moreover, this strategy is especially interesting to avoid an increase in ash content associated with the high burn-off carbon losses throughout activation [35,317]. Moreover, acid treatment has also demonstrated a positive effect on the sulfur content of tire char, for example, Akyildiz et al. [318] used an HCl and HNO₃ mixture for leaching of tire char that resulted in highly efficient desulfurization of tire char (95.3%). However, H₂SO₄ used for tire char

demineralization could provoke the addition of more residual sulfur. The application of alkaline reagents can also promote the removal of certain forms of sulfur in carbonaceous materials [319].

In the physical activation process, tire char undergoes partial gasification using different oxidizing agents, mainly steam and carbon dioxide. The operating conditions usually considered are particle size, temperature, activation agent, and activation time [320,321]. According to different applications, different modification processes are needed. The conventional modification processes of tire char are shown in Fig. 16.

Compared with the original tire char, the particle size of tire char after superfine pulverization decreased significantly and the product powder was closely packed. The finer the particle size was, the easier the particle agglomeration. The production of activated carbon obtained from waste tires is typically divided into two steps: (i) waste tires are pyrolyzed under the condition of the inert gas atmosphere and produce carbon materials, pyrolysis oil, and gas for energy utilization. (ii) The tire char is activated by chemical [322] or physical methods [35]. However, complex processes and low efficiency are the disadvantages of traditional activation methods. According to the application requirement, the modification process of tire char needs to be adjusted to reach the standard specifications required for commercial carbon black.

5.1. Comparison of properties of tire char with commercial carbon black

Carbon is the main component of tire char, and its content in tire char is higher than 80 wt. %. Tire char contains a certain content of ash [204], and the specific surface area is typically $\sim 90 \text{ m}^2 \cdot \text{g}^{-1}$ [21]. According to EDS and XRF analyses of tire char, the inorganic elements in ash include Zn, Si, Al, Na, Ca, and Fe. The content of Si that exists in ash is relatively higher than other elements, up to 3.47% [69]. Some nano-sized particles in tire char coalesce into micro-sized particles. The tire char has uneven size distribution, rough surface, irregular shape, and smaller pores. But, the particle size of tire char is smaller than commercial carbon black (N550) (Fig. 17A) [323].

From Fig. 17Ac, the distribution range of tire char particle size is narrow and the average particle size is 8 μm , whereas for carbon black N550, the distribution range of particle size is wide, mostly ranging from 20 to 40 μm and most of the particles are observed to have a higher particle size of $\sim 40 \mu\text{m}$ (Fig. 17Ad). In addition, very few aggregations are observed in N550 carbon black than that in tire char. The mean primary particle size of commercial carbon is mostly in the nanometer range (from 8 nm to 100 nm) with particles often aggregating in grape-like clusters of size up to 500 nm. Tire char has a developed porous structure, with an average pore diameter of 25–30 nm, with fewer micropores but more mesopores. This phenomenon was also proved in the

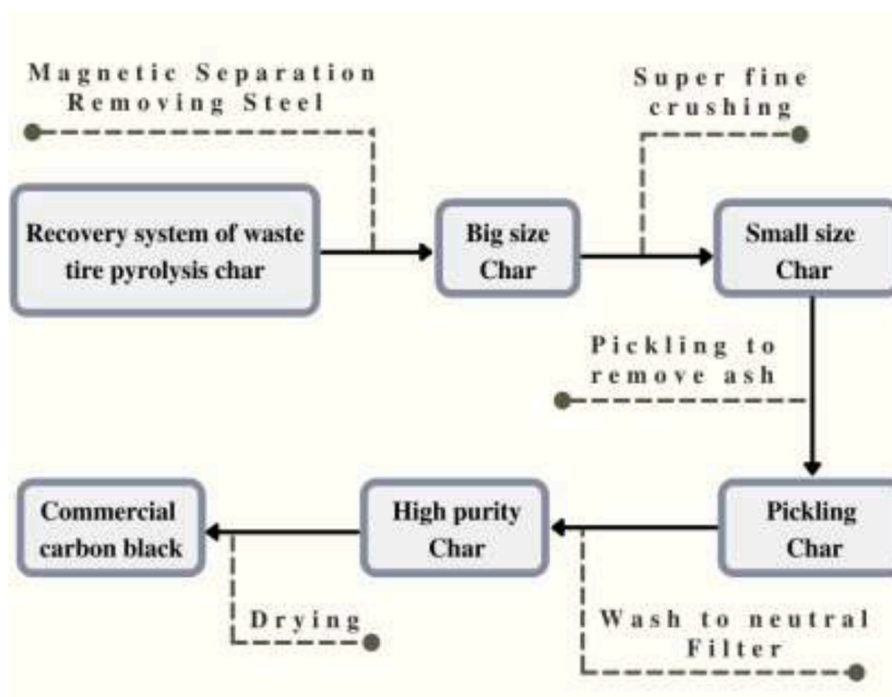


Fig. 16. The flow chart of waste tire pyrolysis carbon black modification process

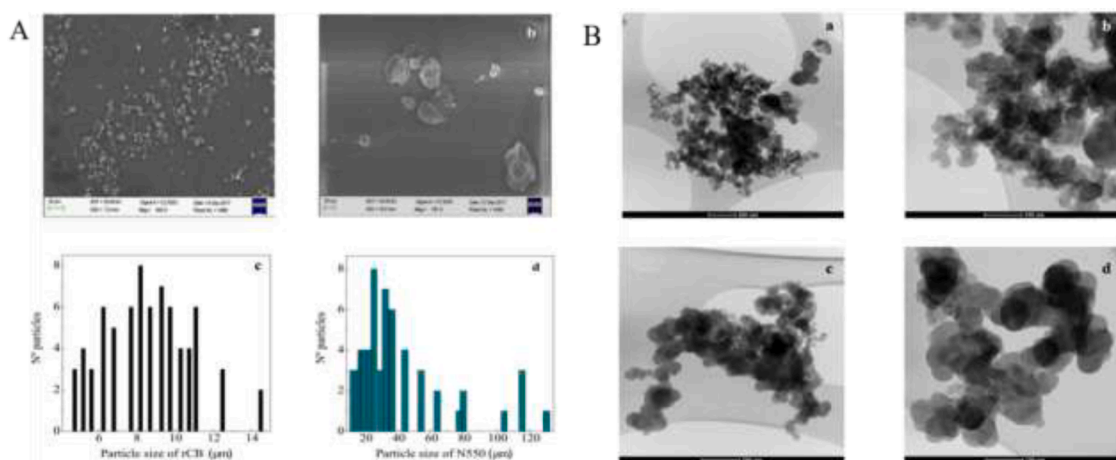


Fig. 17. (A) SEM image of tire char (a) and N550 (b), particle size distribution of tire char (c), and N550 (d) [323]. (B) TEM image of tire char (a, b) and N550 (c, d) [324].

literature by Helleur et al. [278], they compared the particle size of tire char and commercial carbon with TEM photos and indicated that the aggregation of tire char appeared under a low power microscope. However, higher homogeneity was found in commercial carbon black N550 than that in tire char (Fig. 17B) [324]. The tire char as received was odourous, which was because pyrolysis volatiles composed of aromatic rings and ester chemical groups were attached to the surface of the tire char. This also resulted in poor quality and a small specific surface area of tire char. The amount of ash in tire char results in a reduced content of carbon in the tire char, which seriously affects the quality and value of the product char.

The mentioned poorer features compared with commercial carbon black hinder the direct reutilization in tire manufacturing [155,325]. Table 7 compares the properties of tire char with some commercial carbon blacks (N375, N110, rubber carbon black GB 3778-2011, pigment carbon black GB/T 7044-2003, and activated wood carbon for water purification GB/T 13804-2). The components of tire char were

different from that of a commercial carbon black standard. Therefore, untreated tire derived char can be principally used as a low-grade reinforced filler in the production of low-quality rubber and as pigment for ink [326]. In this scenario, different alternatives have been proposed to improve char quality and ease its reutilization as carbon black. The simplest approach is the optimization of the pyrolysis process conditions to improve char quality, in this respect, the operation under vacuum conditions has demonstrated promising results by reducing residual carbon black adulteration [93,302]. Tire char demineralization is another common strategy for char upgrading. Thus, the structure of the tire char is modified by removing ash and improving the relative mass of carbon in the tire char, expanding the pores and increasing the specific surface area of the tire char and has the potential to be used as a high-value commodity and used to obtain more value [327]. In spite of the suitable demineralization efficiencies reported in the literature using acid treatments [316,318], the modification in char surface properties associated with the oxidation under concentrated acids, such as HCl and

Table 7
The component properties of tire char and commercial carbon black.

	Tire char						Rubber carbon black		Pigment carbon black	Activated carbon
	ar	db	db	ar	db	db	N375	N110	(C111)	for water purification
Proximate analysis (wt.%)										
M	1.02	-	-	0.09	-	-	-	-	-	-
FC	87.55	86.4	89.3	90.8	78.61	81.75	-	-	-	-
V	4.89	3.7	1.77	0.67	5.58	3.36	-	-	> 3.0	-
Ash	12.21	9.9	7.93	7.41	15.81	14.89	-	-	< 0.5	-
Ultimate analysis (wt.%)										
C	83.01	70.77	89.33	90.27	78.83	79.45	97.26	96.01	-	-
H	0.38	0.76	0.35	0.26	1.51	0.60	0.33	0.26	-	-
N	0.40	-	0.15	0.16	0.38	0.35	0.35	-	-	-
S	4.52	3.05	2.3	1.22	2.98	3.39	0.57	-	-	-
O	-	25.42	7.87	-	16.30	16.21	-	-	-	-
BET surface area (m ² ·g ⁻¹)	77.63	-	49	63	-	50.03	86-100	120-134	200-600	-
Absorbing iodine value (mg·g ⁻¹)	-	-	-	-	-	161.97	90± 6	145± 8	-	> 800
Particle diameter (nm)	14-36	-	-	-	-	-	-	-	9-37	80
Liquidity (35°C·mm ⁻¹)	-	-	-	-	-	-	-	-	> 16	-
pH	-	-	-	-	-	-	-	-	2.0-6.0	7.0-11.0
Heating loss (wt.%)	-	-	-	-	-	1.54	≤ 2.0	≤ 3.0	< 6.0	-
Tinting	-	-	-	-	-	-	107-121	115-131	> 109	-
Methylene blue discoloration (mg·g ⁻¹)	-	-	-	-	-	-	-	-	-	> 6.0
Refs.	[36]	[329]	[204]	[72]	[138]	[288]	GB 3778-2011	GB 3778-2011	GB/T 7044-2003	GB/T 13804-2

ar: As received basis; db: Dry basis.

HNO₃ represents a significant challenge for their reutilization after leaching [328]. From Table 7, compared with the commercial carbon black, the current research on tire char is relatively shallow. In the past, the study of tire char mainly focuses on the observation and research of basic analyses such as proximate analysis and ultimate analysis. However, there are relatively few other performance tests reported for tire char. Currently, researchers are beginning to pay attention to the industrial characteristics of tire char. However, there is a certain deviation from the research matched to the characteristics of commercial carbon black. In future research, more attention should be paid to the characteristics and application performance of tire char related to the required specifications of the end-use.

5.2. CO₂ physical activation

Gas activation of tire char for the production of activated carbons is usually performed with steam or CO₂ at temperatures above 800 °C. It is worthy of note that CO₂ activation requires higher temperatures than that of steam (H₂O) due to the slower reaction rates attained with the former activation agent moreover, steam also has a better capacity for the development of micropores [264]. The different behavior of CO₂ and H₂O lies in the smaller molecular size of water, which facilitates diffusion within the porous structure of the char [330]. However, air used as an activation agent is limited due to the fast reaction rate and difficulty to control the process.

CO₂ is a major gas that contributes to global warming. Therefore, the use of CO₂ is an activation agent for tire char, not only activates tire char but through this utilization also provides an alternative to the release of CO₂ to the atmosphere and represents an environmentally friendly way to deal with CO₂. Betancur et al. [286] proposed and studied the direct pyrolysis and activation of waste tires in a CO₂ atmosphere. When the temperature was lower than 760 °C, the pyrolysis characteristics of the waste tires in the CO₂ atmosphere were similar to that in an N₂ atmosphere. When the temperature was higher than 760 °C, the redox reaction occurred between tire char with CO₂:



The activation reaction mechanism of tire char with CO₂:



The CO generated in the reaction could briefly cover the reactive activation site, which prevents the further reaction between tire char and CO₂, and reduces the loss rate of carbon in tire char [331]. When the temperature is higher than 900 °C, tire char was activated in the CO₂ atmosphere [322] and the specific surface area could reach 414 m²·g⁻¹, these results were similarly reported elsewhere in the literature [332]. The main factors influencing the activation process of tire char are temperature, activation time or burn-off, particle size, and the CO₂ partial pressure [35]. The main reason for the increase of the specific surface area of CO₂ activated char is the small pore size development throughout the activation of the product and high pore volume. Tire char was activated with CO₂ at the final temperature of 950 °C, and the produced activated carbon had a specific surface area of 437 m²·g⁻¹ [36]. There are many reports in relation to kinetic models of tire char activated in a CO₂ atmosphere, describing the reaction rate versus conversion curve [28,333].

5.3. Steam physical activation

Tire char physically activated with steam produced not only high-quality activated carbon but also hydrogen-rich syngas. Many studies have reported that steam activation was an efficient activating process in the activation field of tire char [334,335]. Moreover, the use of steam as an activation agent also contributes to the sulfur reduction in the obtained carbon [336], this point is of great interest for the final application as activated carbon.

The high specific surface area of activated carbon obtained from tire char under a steam atmosphere has been reported to be as high as 1260 m²·g⁻¹, however, the yield of the product activated carbon was only 9 wt. % [337]. According to the results from Merchant and Petrich [294], the yield of activated carbon was 60 wt. %, and the specific surface area of the tire derived activated carbon was 500 m²·g⁻¹ at 850 °C produced in an atmosphere of nitrogen: steam of 1:5. A specific surface area of steam activated tire char of 272 m²·g⁻¹ with a carbon burn-off of 25.9 wt. % at 900 °C was reported [278]. In another study, the specific surface area of activated carbon from waste tires was 985 m²·g⁻¹ with a

burn-off of 65.0 wt. % [305]. The relation between the specific surface area and carbon burn-off of tire char with steam activation at 850 and 900 °C was analyzed and reported [336] (Fig. 18).

The activation reaction mechanism of tire char with H₂O has been proposed [338]:



This activation reaction mechanism could be confirmed by the results of activation syngas analysis [339]. In the steam activation, the specific surface area of the char was 786 m²·g⁻¹ with 78.4 wt. % burn-off. This result is better than that reported in the literature using CO₂ as the activating agent using [336].

5.4. Chemical activation by impregnation methods

Impregnating tire char with a chemical reagent has the potential to remove the inorganic matter of the ash of tire char, enlarge the pore diameter, improve the relative content of carbon, and increase the specific surface area of tire char [36,340]. A wide variety of chemical activation agents have been proposed in the literature for activated carbons products such as alkali hydroxides (NaOH/KOH), inorganic acids (H₃PO₄, HCl, and H₂SO₄), or ZnCl₂ [35]. Some metallic and non-metallic elements in the ash of tire char can be dissolved in HCl, and the ash content of tire char modified by HCl is also reduced correspondingly [341]. The surface of tire char modified with H₂SO₄ exposed several loose surfaces. As H₂SO₄ has a strong corrosive effect, some pores inside the activated char are cross-linked by acid corrosion, so that small pore connections become larger pores, thereby increasing the specific surface area [273]. After impregnation with NaOH, the quality of tire char was improved, for example, the sulfur content in tire char modified with alkali washing was significantly decreased, but the content of oxygen was increased. The surface area was 215 m²·g⁻¹ with an increase in the micro-pore ratio [26]. The characteristics of activated carbon from tire char with NaOH and KOH solution were reported [342], and their specific surface area reached 738 m²·g⁻¹ and 951 m²·g⁻¹, respectively. The removal rate of ash and sulfur in tire char modification was investigated [343] using HCl and HF under the conditions of ultrasound processing. The ash in tire char was mainly composed of metal oxides, sulfides, and silica. The modified tire char produced was similar to commercial carbon black in terms of surface properties, porosity, and morphology, which could be an alternative product for commercial carbon black N326 for making tire rubber. Only

1.2 wt. % ash in the char was reported with HCl leaching. After upgrading with HCl, the specific surface area was 76.3 m²·g⁻¹ and most ash components were removed [324]. Heras et al. [344] used nitric acid (HNO₃) as a cyclic activator to increase the specific surface area of tire char to 750 m²·g⁻¹, which provides a reference for tire char activation technology.

In summary, Table 8 shows that, different activation methods have different effects on the tire char. The specific surface area of activated carbon varied from 90 to 1317 m²·g⁻¹, which depended on activation method, carbon burn-off, activation time, temperature, gas flow rate, etc [278,334,339,348,349]. Some researchers reported that the activated carbon obtained from the steam activation of tire char had better quality than that from CO₂ activation at certain conditions, since the molecular size of steam is smaller than that of CO₂ [350,351]. Except for steam and CO₂, tire char could also be modified using NO and O₂ [352]. However, the quality of the activated carbon product was determined by various factors, which not only depended on the activation agent.

The quality and characteristics of activated carbon derived from tire is not only related to the composition of tire char but also related to the more complicated activation technology. Activation produces open pores, expansion and generation of new pores, therefore, developing the existing pores of the tire char. Comparing gas activation and chemical reagent activation, there are no chemical reagents and secondary washing processes in the gas activation process. Also, the quality of activation tire char by physical activation depends on high temperature and long residence time. There is no equipment corrosion and environmental pollution in the gas activation process. The tire activated carbon from the gas activation process can be used directly. However there is a need to improve the speed of reaction, shorten the reaction time, and reduce energy consumption as key issues that need to be solved in the gas activation process. The temperature of chemical reagent activation is usually lower than that of physical activation. The largest disadvantage of chemical reagent activation is the reagents used are usually corrosive to equipment. The product activated carbon needs to be washed to neutrality after chemical reagent impregnation activation of tire char, which may cause significant water pollution. Therefore, the overall cost of the process is markedly increased and hinders its implementation at a large scale [353]. Reagents could remove the ash in the tire char, but physical activation could not. The single activation modification technology has some drawbacks, for example, activated carbon with a high specific surface area has a large burn-off using a steam atmosphere, and the ash content in activation tire char is high in the gas activation process. Mixtures of activation methods could improve the quality of activated char and decrease the burn-off and

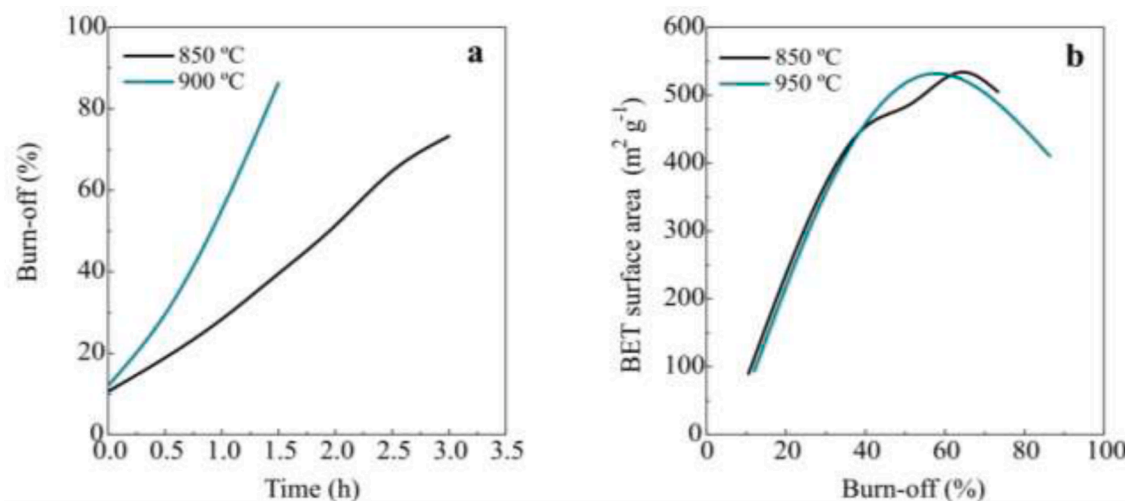


Fig. 18. (a) Evolution of burn-off in the activation process at the two temperatures studied. (b) BET surface area values of the active carbons obtained at different burn-off levels [336].

Table 8
Comparison of the modification of tire char.

Method		CO ₂	H ₂ O	HCl+ H ₂ O	HCl+ CO ₂	Chemical reagent Acid solution		Alkaline solution		Fenton
Experimental condition	Temperature (°C)	750-950	750-920	850-950	800-950	20	70	Room temperature	Room temperature	20
	Dosage	0.05-5 L·min ⁻¹	0.6 L·min ⁻¹ - 3 kg·h ⁻¹	1 mol·L ⁻¹ HCl	1 mol·L ⁻¹ HCl	tire char/HNO ₃ (15-65 %) 1g/10 mL	2-4 mol·L ⁻¹ HCl	1-3 g/g (tire char/NaOH)	1-3 g/g (tire char/KOH)	tire char/H ₂ O ₂ (15-35 %) 1g/10 mL
	Active time (h)	1-3	1-4	Acid wash 24 h + H ₂ O (1-4 h)	Acid wash 2-16 h + CO ₂ (1-4 h)	24	3	24	24	24
Advantages		Simple production process, no equipment corrosion, combustion gas generated, low environmental pollution.		combustion gas generated, low ash content, high carbon content.		Low tire char loss, high carbon content, low ash and sulfur content.		Low sulfur content, higher S _{BET} and Iodine.		Higher S _{BET}
Disadvantages		High temperature, energy consumption, and cost, ash content high, slow reaction rates.		Equipment corrosion, complex process, long time, energy consumption, high cost.		Equipment corrosion, complex process, long time.		Equipment corrosion, complex process, low carbon content, high hydrogen and oxygen content.		
Proximate analysis of tire char (air dry basis)										
M (wt.%)		-	-	-	-	-	-	3.16-4.35	3.45-4.12	-
FC (wt.%)		-	-	-	-	-	-	78.63-80.82	76.09-80.59	-
V (wt.%)		-	-	-	-	-	-	10.65-13.78	10.05-14.16	-
Ash (wt.%)		12.68-14.36	11.9	18.3	2.7	-	1.26-3.30	4.18-5.88	5.69-5.91	-
Ultimate analysis of tire char (air dry basis)										
C (wt.%)		81.35-84.52	-	-	95.67	-	95.55-96.12	71.99-75.3	72.55-76.44	-
H (wt.%)		0.10-0.20	-	-	0.11	-	0.11-0.20	2.41-8.04	2.67-3.49	-
N (wt.%)		0.14-0.15	-	-	0.18	-	0.12-0.20	1.14-1.40	1.40-2.24	-
S (wt.%)		2.55-4.87	-	-	1.33	-	0.96-1.19	0.16	-	-
O (wt.%)		-	-	-	-	-	-	12.26-25.15	19.49-21.79	-
Burn-off (wt.%)		6.0-61.0	9-87.5	33.1-78.6	-	12-90	-	-	-	7-89
S _{BET} (m ² ·g ⁻¹)		99-483	154-1317	585-1177	203-1014	100-750	-	116-700	798-951	95-400
Iodine (mg·g ⁻¹)		146-302	234-277	-	-	-	-	556-720	635-752	-
Refs.		[286,334,345,346]	[334,339]	[33]	[345,346]	[344]	[345]	[26,342,347]	[342]	[344]

- not described in the reference text.

activation cost [354].

6. Applications of tire char

The global annual increase in the yield of waste tires, with their associated very low or even negative cost as a process feedstock, makes the consequent cost of producing tire char low, which is also the main reason for the rapid growth of the tire char market. Due to the different sources and pyrolysis processes of waste tires, tire char accounts for 30-37 wt. % of tire pyrolysis products, with an ash content of about 7.0-15 wt. %. There are many applications that have been suggested for the use of tire char. For example, printing ink is a colloid dispersive system that is composed of filler, linking material, pigment, and auxiliary agent, where tire char could be used as pigment added to printing ink [355]. For example, the performance of tire char as a pigment in offset printing ink has been reported [356]. The application of tire char as solid fuel has also been reported in the literature [357]. It was also suggested that tire char could be used as filler in modifying asphalt [358,359]. The specific surface area, pore diameter, and surface properties of tire char are also different when obtained under different tire pyrolysis conditions [360]. Tire char has the characteristics of developed pores and small pore diameters. However, due to its low specific surface area, it cannot meet the application requirements of commercial carbon black. Thus, its economic value is relatively low [250,361]. Therefore, attention is focused on how to effectively increase the added value of tire char. At present, the applications of tire char are wide and these utilization alternatives are represented in Fig. 19. The main application includes activated carbon as adsorbents prepared by modifying tire char [351], rubber reinforcing materials (commercial carbon black) [362], battery

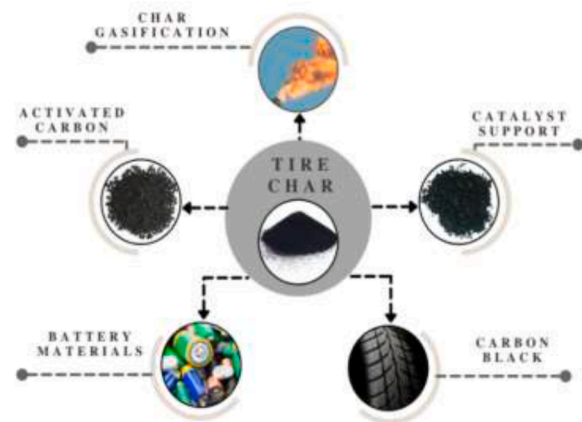


Fig. 19. The main high added value applications of tire char.

materials, catalyst support materials, and asphalt additives [187].

6.1. Tire char gasification for fuel gas

Tire char could be gasified with steam and carbon dioxide to produce a fuel gas due to the high carbon content of tire char. In Sections 5.2 and 5.3, the gasification mechanism with CO₂ and steam was discussed. The products of gasification are used as fuel gas, which has a high heating value, and its use results in low secondary pollution. Moreover, the use of steam as a gasifying agent allows for hydrogen-rich gas production.

Tire char showed higher reactivity with steam than that with CO₂ [276]. The low reactivity of tire char with CO₂ also was investigated in different reports [363,364] (Fig. 20). The activation energy of tire char in the CO₂ atmosphere was 250 kJ·mol⁻¹ reported by Pooya et al. [363], while, it was 57.06 kcal·mol⁻¹ reported by Jung et al. [364]. Carbon conversion has a crucial relationship with high temperature, the high temperature increased the carbon conversion rate and decreased the time for complete carbon conversion. The data (Fig. 20) show that the reaction time of 40 min was rather long even at a high temperature (1000 °C) in the CO₂ atmosphere, and it can be shorted to about 20 min for a high carbon conversion through the co-gasification of tire char and other bio-char.

Carbon conversion reached 1.0 required a reaction time of 2.8 h at the condition of 10 vol.% steam and 900 °C [349]. The initial weight (10-15 mg) did not show any remarkable influence on the carbon conversion in TGA experiments in the steam atmosphere. Without considering the initial weight, the gas atmosphere, activator dosage, and temperature are the main factors affecting the carbon conversion time. Because the initial weight of tire char was only 8 mg and with a 50 ml·min⁻¹ CO₂ flow rate in the gasification of tire char at 1000 °C, the reaction time of 40 min reported by Pooya et al. [363] was shorter than that in the report by Aranda et al. [349]. However, more time was needed to reach carbon conversion when the initial weight was increased to 5 mg [365], requiring 4 h when the carbon conversion could only reach 60% at 950 °C with 66.7 vol.% steam. Carbon conversion was around 30-70 % higher for steam activated chars than for CO₂-activated chars between 950 and 1050 °C. This showed that steam activation yielded higher carbon conversion than that with CO₂ activation under the same activation conditions. The activation energy required for tire char gasification using steam was lower than that with CO₂ [349]. The results indicated that a higher syngas yield was generated with steam gasification at high temperatures, which could reach 86 wt. % at 1000 °C and produce a product gas with a 25 MJ·kg⁻¹ heating value [366]. The gasification of tire char is a two-way process. Excessive gasification of tire char will convert all the carbon into fuel gas. When the carbon conversion of tire char reached 70-80% [365], it not only produces a high yield fuel gas but also obtains a high quality activated carbon. The activation energy of tire char in a steam atmosphere could reach 114.3 kJ·mol⁻¹. The specific surface area of gasification tire char increased 80% compared with the initial specific surface area of tire char.

Although there are many studies on tire char activation to generate fuel gas, most of the research focuses on the carbon conversion and activated energy of the tire char. It is difficult to find literature to calculate the lower heating value of fuel gas generated from tire char activation, let alone the energy analysis of tire char activation.

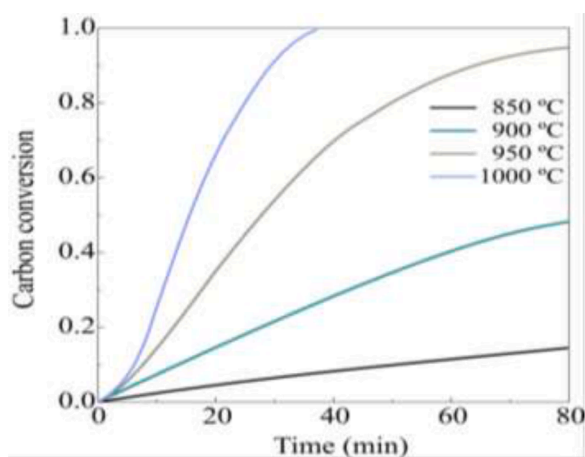


Fig. 20. Carbon conversion of tire-char at several gasification temperatures with TGA [363].

6.2. Tire char as adsorbent (activated carbon)

Compared with other technologies of wastewater treatment (reverse osmosis [367], ion exchange [368], extraction (liquid-liquid) [369], electrodialysis [370], and electrolysis [371]), adsorption has the advantages of low treatment cost and easy operation [372]. The quality and cost of adsorption materials have a great influence on the effect of wastewater treatment. Carbon materials have been widely used in removing harmful substances that exist in industrial wastewater and waste gas because of their cheap and wide resource availability [373]. Usually, activated carbon used in liquid adsorption applications should be mesoporous materials. It has been widely demonstrated that activated tire char is mesoporous, the application of chemical and physical activation processes may further develop the tire char porous structure. Tire derived carbon materials could be used as an adsorbent [334,351] in removing harmful substances that may exist in wastewater. Augustine et al. [309] prepared tire char and studied the characterization of tire char for removing copper. The removal rate of copper could reach 24 mg·g⁻¹ with tire char. The maximum adsorption capacity of methylene blue reached 120 mg·g⁻¹ with activated tire char [374].

Guerrero-Esparza et al. [375] adjusted the pyrolysis process of waste tires and modified the product tire char. The adsorption of Fe ions in water by modified tire char was also studied. The results indicated that the specific surface area of tire char is the main factor affecting the adsorption of Fe ions. The oxygen electrons on the surface structure of tire char (carbonyl, carboxyl, ester) electrostatically interact with Fe, which enables Fe ions to enter abundant adsorption sites, thus increasing the adsorption performance of tire char for Fe ions. The adsorption of organic compounds 1,3-dichlorobenzene (DCB), 1,3-dinitrobenzene (DNB), and 2,4-dichlorophenol (DCP) by using tire char has been investigated [376]. The results showed that tire char had a good adsorption effect on organic matter, and the specific surface area of the char was the main factor affecting the adsorption quantity. The treatment capacity of methylene blue between acid-treated activated tire char and commercial carbon was compared [316]. It was reported that the adsorption capacity of activated tire char was higher than that of commercial carbon. The adsorption capacity of Cd (II) and Pb (II) could reach 201 and 196 mg·g⁻¹ respectively with chemically activated tire char [377]. After regeneration, the chemically activated tire char could be used repeatedly ten times, before the adsorption capacity decreased. According to Makrigranni et al. [378], the maximum adsorption capacities of phenol and methylene blue on acid-treated tire char were found to be 51.92 mg·g⁻¹ and 65.81 mg·g⁻¹, respectively. KOH-treated tire char, with a surface area as high as 700 m²·g⁻¹, presented maximum adsorption of tetracycline of 312 mg·g⁻¹ [379].

The use of tire char as commercial activated carbon after pretreatment and activation using different strategies has been widely investigated, especially in wastewater treatment. The efficiency and capacity of its use in wastewater treatment are remarkable, which reinforces its potential application as an adsorbent.

6.3. Tire char as supporting material and catalyst

The catalyst support material plays an important role in the preparation of catalysts. The properties of the support materials affect the loading capacity, the interaction between the active phase and support, and the dispersion of active components. Modified tire char has some characteristics, such as light weight, soft texture, small particle size, and large specific surface area that demonstrate its potential as a catalyst support material. The influence of tire char as support material was studied by Zhang et al. [380] for supported platinum catalyst in relation to the yield and composition of methyl cyclohexane cracking products. The results showed that platinum had a good loading capacity and dispersion on the modified tire char, and formed Pt nanoparticles with a particle size of about 2.5 nm, which were well dispersed on the surface of the modified tire char. The catalyst activity was mainly influenced by

the capacity of Pt and temperature. The conversion rate of methyl cyclohexane to hydrogen and toluene was up to 95 %. Ji et al. [381] prepared heterogeneous catalysts supported by two chiral Mn (III) complexes on tire char, which had a good catalytic performance in the asymmetric epoxidation of nonfunctional olefin with a conversion rate of 99%. For the asymmetric epoxidation of 1-phenyl cyclohexene, the two heterogeneous catalysts synthesized had better catalytic performance and higher enantio-selectivity than the homogeneous catalyst, which could be recycled three times. Sulfuric acid was used [382] as the source of the SO_3H group to load on tire char and was investigated for the transesterification and esterification of waste oil under subcritical conditions. Compared with other reported literature, the tire char catalyst had the advantage of short reaction time and low energy consumption.

Catalysts have been widely used in the reforming of pyrolysis oil, increasing the yield of pyrolysis gas. The effect and mechanism of tire char in the oxygen reduction reaction for alkaline fuel cells were reported in the literature [383]. The large specific surface area and porosity of the tire char were the main factors contributing to the enhanced oxygen reduction reaction (ORR) activity. The high concentration of ZnO in the tire char was another factor for enhanced ORR activity. This study showed that tire char could be easily transformed into a high performance and stable electro-catalyst for the ORR. Heated tire char increased the quality of waste tire pyrolysis oil and gas [24]. The yield of the waste tire pyrolysis gas could reach 10.5 wt. % after catalytic pyrolysis with a heated tire char, which was significantly higher than that without catalysts. A high yield of single ring aromatic compounds was obtained at the catalytic condition with the heated tire char. Tire char could be used as a catalyst in the waste tire pyrolysis process and could decrease the production of large-size aromatic compounds in the product pyrolysis oil due to its mesoporous structure [121], the effect of acid-treated tire char was higher than that of tire char. The effect of tire char on the decarboxylation and dehydration of bio-oil was studied [292], the extent of deoxygenation of bio-oil could reach 40.3 wt. % under the conditions of tire char loading of 80% in the catalytic process. ZnS in tire char played a positive role in the catalytic reaction. Tire char also appeared in a positive role in biomass gasification, the yield of hydrogen could reach $39.20 \text{ mmol}\cdot\text{g}^{-1}$ with the use of tire char [384].

6.4. Tire char as reinforcing agent for tire rubber

Carbon black plays a reinforcing role in rubber processing, which is an important member of the reinforcing system. Carbon black added to rubber could also improve rubber wear resistance and reduce industry costs. The characteristics of tire char have a certain similarity with commercial carbon black, which provides support for its use as a rubber reinforcing additive. Tire char has a small particle size, so it would have good dispersion in rubber [385]. Modified tire char has a reinforcing effect, which enhances the mechanical properties of rubber, such as tensile strength and hardness [323]. However, tire char as a reinforcing agent represents a significant challenge due to the impurities present. Tire char was used [386] as the reinforcing filler for SBR, which would not affect the solidification of rubber. The good dispersion of tire char makes the tear strength and fracture mechanical properties of SBR higher than that of commercial carbon black added as N330, which leads to the expansion of the damaged area at the crack tip of the binder. In the comparison of tire char with N330, it was found that the good trend of tearing characteristics is an additional effect of the dispersion of tire char. In terms of other properties, tire char has some similar properties to commercial carbon black and could be a potential alternative. The performance of tire char used with ethylene-propylene rubber was investigated [323] and it was shown that the reinforcing effect and the cross-link density of tire char were good but slightly lower than that of commercial carbon black (N550). The function of acid-treated tire char as an additive in styrene-butadiene rubber was investigated [324], the

poor mechanical properties of SBR added with acid-treated tire char were ascribed to the presence of higher mineral matter and poorer structure in tire char. Despite these negative properties, it was demonstrated that acid-treated tire char showed relevant reinforcing effects. Tire char separated from the cross-linked network of ground tire rubber demonstrated an excellent reinforcing effect on solution styrene-butadiene rubber [387].

6.5. Tire char as battery and capacitor material

Super-capacitors and batteries are devices for storing energy and are used in electric cars, mobile phones, computers, nano-generators, and other electronic equipment [45,388]. At present, the research on activated carbon-based capacitors has attracted much attention, especially carbon nanomaterials as capacitors, have been widely studied owing to their exceptional combination of intrinsic properties. Carbon nanomaterials can be used as both matrices and functional additives due to their miscellaneous structures and dimensionality ranging from 0D to 3D. And most notably, their tunable surface chemistry and versatile surface functionalization has led to important roles in charge-transfer systems and trending energy sources [389]. The electrochemical performance of carbon nanomaterials was usually enhanced by doping heteroatoms. Xiaoqiang et al. [390] designed and prepared a nano-silica/carbon hybrid matrix layer on silicon nanoparticles as anode materials for lithium-ion batteries. With the introduction of nano-silica, the multifunctional nano-silicon/carbon hybrid matrix can significantly maintain structural integrity during the volume change of silicon, provide a higher capacity than the traditional single carbon coating layer and enhance the conductivity of the materials. Carbon-based materials have been widely promoted due to their good electrical conductivity and chemical stability. The characteristics of boron-doped graphene aerogels (B-Gas) prepared through the hydrothermal method were reported in the literature [391]. The combination of mesoporous structure, high specific surface area, and abundant defects of B-Gas enhanced the performance of super-capacitors. The cost of traditional carbon materials (carbon paper, carbon cloth, and graphite) is expensive, which limits their wide application. The costs of using the waste tires for processing are cheap, while tire char as electrode materials could increase the economic viability of the waste tire treatment process [392].

There are many advantages of tire char, specially modified tire char with a high specific surface area, high conductivity, and other characteristics. The characteristics of modified tire char meet the requirements of super-capacitor materials, which could be an ideal electrode material for super-capacitors. Activated tire char displayed good electrochemical properties [393] and were demonstrated as suitable material for super-capacitors. The highly porous carbon from the waste tire was produced and used as a super-capacitor with long cycle life [394]. Shilpa et al. [395] removed the ash in the tire char and obtained a high purity carbon by using hydrochloric acid (HCl) and hydrofluoric acid (HF) processing. The tire char was further activated by potassium hydroxide (KOH) to adjust the surface characteristics of carbon, producing an activated carbon of a specific surface area of $870 \text{ m}^2\cdot\text{g}^{-1}$. The processed carbon was used as an anode of lithium-ion batteries, whose high specific capacitance reached $880 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ with 80% of the capacity retention after 100 times recycling. Activated carbon from tire char was used as super-capacitor material [396] and the effects of physical characteristics (pore size, etc.) of activated carbon on the capacitance and charge and discharge rate of super-capacitor materials were studied. The results showed that the capacitance of activated carbon was controlled by micropore volume, the charge and discharge rate was greatly influenced by the volume ratio of mesopore with micropore and has nothing to do with the absolute value of mesopore volume. Naskar et al. [397] produced tire char, with a high content and ordered assembly of graphite, from tire rubber pretreated with a hot oleum bath and pyrolysis under a nitrogen atmosphere. The reversible capacity of the cell with the char used as the anode was $390 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 100

cycles, with nearly 100% coulombic efficiency. Li et al. [398] reported the influence of pyrolysis temperature on the energy capacities of tires and then used the char as an anode for sodium-ion batteries. But the result, with the best capacity of 203 mA·h·g⁻¹ after 100 cycles, was worse than that reported by Naskar et al. [397].

6.6. Tire char applications in construction and materials

In spite of the fact that tire crumb has been widely used as a concrete additive to improve its mechanical properties [399–401], the positive features of tire char as reinforcements for concrete were recently reported by Mahmood et al. [402]. The addition of only 1.0% to concrete formulation enhanced the fracture toughness of treated concrete by 48.8%. At the same time, the compressive strength was remarkably improved (49%) after tire char incorporation.

The use of tire char for the production of phase change materials (PCM) was proposed [403,404], which could be used as an additive to cement mortar. PCM materials have the ability to accumulate heat and ensure a high energy storage capacity which is of special relevance for energy-saving construction. In this respect, the use of tire char showed a promising performance in the application as PCM which allows for the development of new and sustainable heat-accumulating building material for application in the construction industry.

Another relevant application of tire char in the construction sector is the production of road bitumen as a binding agent used for road pavements, parking areas, and driveways. It is notable that the incorporation of tire derived char demonstrated a capacity to improve the rheological properties of bitumen [405–408]. A positive effect of tire char addition to bitumen has also been reported [409], apart from improving the rheological properties, it enhances the electrothermal properties of

bitumen, making the modified binder feasible for multifunctional applications. Moreover, pyrolysis char addition also contributes to improving thermal and photo-oxidative ageing resistance of bitumen. Thus, Feng et al. [407] performed a complete ageing study of asphalt binders incorporating tire char employing penetration, ductility, softening point, and viscosity tests prior to and after thermo-oxidative ageing and photo-oxidative ageing. Tire char addition demonstrated a remarkable improvement in ageing resistance in relation to unmodified binders. Also, the potential of tire derived char as sustainable asphalt binder modifiers was reported, where the ageing properties and basic mechanical features were improved [410].

Another field of application of tire char is composites production. A composite of low density polyethylene and tire char with different potential applications was reported [411] and showed that the produced composites demonstrated excellent mechanical and dielectric properties. Moreover, tire char was used for the production of castor-based polyurethane composites with promising results [412]. Pyrolytic tire char was used as a carbon precursor in silicon carbide production where the process was carried out in a plasma reactor and showed tire char with a promising performance in this novel application [413].

Table 9 summarized the applications of tire char and some key performance parameters reported in the literature. From the applications of tire char as an adsorbent, catalyst carrier, and energy storage material, it is required for the char to be activated and expanded to increase the specific surface area to achieve better adsorption, catalytic, and energy storage effects. The process of gasification of tire char to produce fuel gas cannot only produce combustible gas but also obtain activated carbon with a high specific surface area. Tire char can be directly used as a filler without activation because char as an additive exists in tire rubber. As asphalt modified material, tire char can be used

Table 9
The application of tire char and key properties.

Application	Gasification for fuel gas	Adsorbent	Catalysts	Supporting material	Reinforcing agent for tire rubber	Battery and capacitor material	Printing ink	Filler in modifying asphalt
Ultimate analysis of tire char (air dry basis)								
C (wt.%)	86.58-87.9	-	74.6-82.5	-	72.9-88.0	82.1-95.5	-	-
H (wt.%)	3.33	-	0.8-1.06	-	1.5	-	-	-
N (wt.%)	-	-	0-0.49	-	0.4	-	-	-
S (wt.%)	-	-	2.46-4.0	-	2.5-3	0.5-1.1	-	-
O (wt.%)	-	-	12.7	-	10.29	3.6-14.8	-	-
Proximate analysis of tire char (air dry basis)								
M (wt.%)	0.1-1.65	-	3.5	-	-	-	-	1.1
Ash (wt.%)	10.3	-	13.3	-	13.2-22.0	-	16.18	18.7
V (wt.%)	-	-	4.2	-	4.7	-	-	4.4
FC (wt.%)	-	-	79.0	-	82.1	-	-	76.9
S _{BET} (m ² ·g ⁻¹)	800-1100	50-814	59-80	57-116	46.1-75	72-190	69.23	-
HHV (MJ·kg ⁻¹)	7.4-34.32	-	-	-	-	-	-	-
Conversion	1.0	-	-	-	-	-	-	-
Time (min)	60-100	-	-	-	-	-	-	-
Activation time (min)	-	50-352	-	-	-	-	-	-
methylene blue (mg·g ⁻¹)	-	8-120	-	-	-	-	-	-
Tetracycline (mg·g ⁻¹)	-	28-312	-	-	-	-	-	-
Phenol (mg·g ⁻¹)	-	3-48	-	-	-	-	-	-
Copper remove (mg·g ⁻¹)	-	5-24	-	-	-	-	-	-
char size (um)	-	-	-	-	2-15	-	-	-
specific capacitance (F·g ⁻¹)	-	-	-	-	-	200-480	-	-
Capacitance (m·Ah·g ⁻¹)	-	-	-	-	-	203-390	-	-
blackness	-	-	-	-	-	-	2.17	-
Jetness value	-	-	-	-	-	-	342	-
Fluidity (mm)	-	-	-	-	-	-	26.5	-
Viscosity (pa·s)	-	-	-	-	-	-	3150	-
Refs.	[276,364]	[309,374,378,379]	[24,121,292]	[380-382]	[323,324,385,386]	[393,394,396-398]	[355,356]	[358,359]

- not described in the reference text.

directly without activation and can still meet the performance of asphalt materials. At present, researchers have explored the different application performances of tire char, but there is no main performance standard for each application of tire char. The specific surface area is the most discussed factor in various applications. The larger the specific surface area, the better the adsorption, catalytic, carrier load capacity, and battery energy storage performance.

7. Conclusions and prospects

This work summarizes the generation, influencing factors, activation, research results, and applications of tire char. The advantages and disadvantages of waste tire pyrolysis from different reports are also compared. Some conclusions are as follows:

- (1) The pyrolysis process and product recovery of the waste tire are complicated technological processes. The yield and quality of tire char are affected by many factors, for example, the pyrolysis technology, equipment, conditions, and the composition of the raw tire feedstock. Different influencing mechanisms exist along with different influencing factors for the waste tire pyrolysis process.
- (2) There is a need to understand the characteristics of tire char before activation. Because they are the theoretical basis of the modification scheme used for tire char. The aim of tire char modification is to improve the quality of tire char and reach (or surpass) the standardized characteristics of commercial carbon black. Tire char modification can improve the business application performance of tire char, and the economy and market competitiveness of the overall waste tire pyrolysis process.
- (3) Tire char is widely used in many fields. Unmodified tire char could be directly used as a solid fuel and tire rubber reinforcing agent. Tire char could also be directly used as a catalyst material to decrease the operational cost, and improve the quality of pyrolysis oil and gas. The modified tire char with high specific surface area and lower ash content could be used as an activated carbon adsorbent material, catalyst and catalyst support, and capacitor electrode to create higher commercial value.
- (4) Most of the applications of tire char are at the preliminary research stage on a laboratory scale. In the reported studies, there is a lack of detailed technical and economic analysis of waste tire pyrolysis and tire char activation technology. This is a common flaw in the current research study of waste tire pyrolysis.

With the gradual maturity and industrialization of waste tire pyrolysis technology, the quality requirements of pyrolysis products will be higher. At present, the recycling applications of tire char have been developed, which has created a high level of potential economic prospects for the waste tire pyrolysis industry. Despite the progress of waste tire pyrolysis technology and the application of pyrolysis products, many issues need to be resolved to meet different industry requirements. The pyrolysis industry of waste tires and the application of tire char need further improvement in the following aspects:

- (1) Developing an integrated treatment system (pretreatment - feed - thermal cracking - pyrolysis oil refining - pyrolysis gas recycling - carbon black modification) will be the main direction of waste tire processing. It could convert the so-called "black pollution" of waste tires into valuable oil, gas, and char by this technology system, realizing economic, environmental, and social benefits. This strategy is related to a circular economy and sustainable development concepts, and moreover, promotes solid waste resource recovery.
- (2) The waste tire feedstock should be classified by brand or tire structure and then pyrolyzed. This is helpful to improve the product quality of tire char. Some reasonable classification

recycling processes should be planned. In addition, there is also a requirement to reduce system investment and operating costs.

- (3) According to the market demand for commercial carbon black, the pyrolysis process of waste tires and the modification process of tire char should be designed and optimized. The recycled tire char with different particle sizes and specific surface area could be obtained by multi-stage crushing and screening. Regenerated tire char should be classified according to particle size and specific surface area for applications in different fields, which could realize reasonable distribution and resource maximization of tire char.
- (4) Heated tire char could be used as a reforming medium for waste tire pyrolysis volatiles, which is beneficial to the quality improvement of pyrolysis oil-gas and the surface functional group structure of tire char. Tire char could be used as a catalyst or modified to generate high specific surface area activated carbon. Moreover, graphene could be obtained from tire char. The economic analysis of tire char applications should be the future research work.
- (5) Pressurized pyrolysis of waste tires could be used to produce high yield and high quality oil and char products. This may become a major direction for the future development of waste tire pyrolysis.

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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