

*Review***Pyrolysis of waste tyre for high-quality fuel products: A review****Deinma T. Dick, Oluranti Agboola and Augustine O. Ayeni***

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Abstract: Pyrolysis is a thermal conversion of materials at high temperatures in an inert atmosphere. Pyrolysis can be obtained through thermal or catalytic pathways. Thermal pyrolysis is known for its high operating temperature, reaction time, and low oil quality. To subdue these challenges associated with thermal pyrolysis, catalytic pyrolysis of the waste tyre has materialized with the use of a catalyst. Catalytic pyrolysis can convert 60–80% of the waste tyre into pyro-oil having close similarities with diesel fuel. Thus the produced pyro-oil is of better quality and could yield useful chemicals as feedstock in chemical processes and energy-related applications such as electricity generation, transport fuel, and heating source. Therefore, this review reports the advancement and limitations of catalytic pyrolysis of the waste tyre and its future perception when compared to thermal pyrolysis. Factors affecting pyrolysis, cons, and limitations of thermal pyrolysis were discussed. These limitations led to the discussion of catalytic pyrolysis, the effects of catalysts on the product yield, composition, and physical properties. Although the catalytic pyrolysis has advantages over thermal pyrolysis, it has few shortcomings which were presented. Some recommendations to address these shortcomings were also stated.

Keywords: catalytic pyrolysis; waste tyre; pyro-oil; thermal pyrolysis; fuel production; value-added products

1. Introduction

The thermochemical conversion process involves the addition of heat in promoting the chemical transformation of materials into chemicals and energy. Examples of processes involved in the transformation are combustion, slow pyrolysis, torrefaction, fast pyrolysis, flash pyrolysis, and gasification. Environmental degradation caused by pollution, coupled with the energy crisis, is said to be a devastating problem for humanity today. The inception of these problems can be attributed to

ultra-rapid industrialization, a fast-growing population, and the daily generation of solid refuse [1]. The relocation of millions of people to urban areas in the last few decades have been recorded all around the world. Apparently, most of the world's population resides within the city [2]. Inadequate technical know-how in the treating and disposal of municipal solid waste in an environmentally friendly form around the developing world has led to its underutilization. Municipal solid waste can be a useful source of recycled resources, revenue, biomass, and energy if managed correctly and wisely [2,3]. One common solid waste material around the world is vehicle tyre, and issues concerning the handling and disposal of this waste is a significant concern. Worldwide estimation places the annual generation of the waste tyre at over one billion [4] and about 2.5 million tons generated annually in Nigeria [5], which is more likely to increase with the production of automotive cars.

Tyres are complex in structure and composition, hence challenging to recover, reuse, and recycle. The essential components of vulcanized rubber, silica, and carbon black constitute about 80% of the total mass of the tyres. Natural rubbers, high-quality synthetic rubber, steel cord, fibres, and various chemical compounds are incorporated in the production of materials for tyre in the vulcanization process [6]. Due to their non-biodegradable characteristic, waste tyre takes more time as compared to biomass to break down in the natural environment, and their components cannot be readily recovered [7,8]. These waste tyres which are conventionally disposed of in landfills and incineration, are an eyesore and can serve as habitats for vermin and mosquitoes [1]. Besides, the combustion of tyres releases pollutants such as polycyclic aromatic hydrocarbons (PAHs), benzene, styrene, phenols, and butadiene, which are detrimental to human health [4]. In 2000, the European End Life Vehicle Directive proposed the following routine for waste tyres: reduce, reuse, recycle, and finally perform an energy valorization process.

Reusing and recycling can find applications in agriculture—as weights for silage cover sheets, shoemaking—as soles, heels, and straps, communities—as bumpers for garages and recreational equipment. Rethreading is also an excellent way of utilizing old tyres. From the literature, it is reported that only 15% of crude oil is required in producing a rethread as against a new tyre. Notwithstanding, these measures—rethreading and recycling—are not sufficient to deal with the massive number of waste tyre being generated [1]. According to Murugan et al. [9] less than 7% of annual tyre production in the world (excluding combustion, rethreading, or reuse). These methods of reuse, recycle, and rethreading do not utilize used tyres as a good energy recovery material. This has led to an increasing interest in thermochemical conversion techniques for fuel and energy generation [9,10].

A favourable and adequate disposing method of the waste tyre is pyrolysis, an environmentally friendly and efficient way. Pyrolysis is a thermal decomposition process that converts waste tyres into solid residue (char), liquid oil (pyro-oil), and gases at temperatures between 300–900 °C. Despite its efficiency, the conventional thermal pyrolysis is affected by certain limitations. This includes its high-temperature dependency and impurities, such as sulphur in the liquid oil [11]. Hence, catalytic pyrolysis is being developed to overcome the challenges of thermal pyrolysis [2]. Catalysts of various types have been harnessed, including CaC_2 [12], MgO [13], ZSM-5 [14], Ultrastable Y zeolite, USY [15], Cu/HBeta zeolite [16], MgCl_2 [17], $\text{Ca}(\text{OH})_2$ [4] and natural zeolite [18], in catalytic pyrolysis to enhance the quality of liquid oil. The introduction of catalysts has been of great interest due to its influence on the energy input, yield, quality, and composition of high value-added products. The lighter fractions in the oil increased [19], and a decrease in the process energy-inputs was recorded [12]. Sulphur, the major impurity found in pyro-oil, decreased in the presence of the catalysts, up to 80% [14]. It is also reported that the presence of catalysts with

high Brunauer–Emmett–Teller (BET) surface area causes an increase in the cracking rate, thus the production of more gases with high H₂ content [20,21].

An extensive review of the practicability of catalytic pyrolysis; its challenges, limitations, and prospects have been scarcely published, although significant research is being carried out to investigate the unique role of various catalysts in the pyrolysis process and its products. Thus, this report reviews the progress and challenges of waste tyre decomposition via catalytic pyrolysis and its prospects in comparison to thermal pyrolysis. The influence of different catalysts on the quality and quantity of pyrolysis products has been studied in detail against the characteristics of catalysts. The various products from the pyrolysis of waste tyres are elaborated in terms of their process conditions, composition, features, and available applications, as reported in the literature. A possible implementation of the product liquid oils would be as a fuel or as a chemical feedstock. Also, the solid residue by-product can be used as an adsorbent for the extraction of heavy metal pollutants from wastewater and air. The gas product could serve as energy carriers. Despite the possible benefits associated with the catalytic pyrolysis process, limitations such as high energy input due to the low thermal conductivity of tyres, cost of catalyst, and catalyst deactivation and regeneration still abound. Also, the lack of experience in pilot and full-scale units of catalytic pyrolysis poses a challenge. For optimum reactor design, a detailed knowledge of the catalyst deactivation and regeneration is needed in order to successfully compare this process with the non-catalytic function in terms of material and operational cost. Some possible solutions to these limitations include co-pyrolysis with biomass, synthesizing, and regeneration of cheaper catalysts, and optimization of the process.

2. Pyrolysis

Pyrolysis, an endothermic process, is a recycling technique in which materials are converted into liquid or pyrolytic oil, solid residue and combustible gases with the recovery of steel at high temperatures in the absence of reactive gases such as air or oxygen via thermal decomposition [2,10,22]. Doğan et al. [23] also defined pyrolysis as the production of char, pyrolytic oil, and gas in the absence of air at temperatures greater than 500 °C from the thermal degradation of solid wastes. Raw material sources for this process could include agricultural by-products, scrap tyre, municipal solid wastes, plastic materials, and wood wastes. Pyrolysis of waste tyres was investigated at varying temperatures ranging from 350–800 °C. However, optimum temperatures have been found to be between 500–600 °C [24]. Heating rates at 13 °C/min [25], 10–110 °C/min [26] and 20 °C/min [27] and retention times of 90 min [10], 50 min [28], and 20 min [29] has also been recorded in waste tyre pyrolysis. Irmak et al. [30] studied the pyrolysis of passenger tyres at varying temperatures from 30–600 °C. They concluded that increase in heating rate, prolonged the degradation process of the tyre which in turn caused an increase in temperature e.g., 40 °C/min (510 °C) and 5 °C/min (454 °C). However, optimization of the process through reduction of process temperature and retention time is viable. The pyrolysis process can be carried out via thermal and catalytic routes.

2.1. Factors affecting the pyrolysis process

Operational parameters such as temperature, pressure, heating rate, feed particle sizes, catalysis, type of reactor, residence time, and flow rate of inert carrier gas affect the pyrolysis process in terms of product distribution and quality. It is essential to consider the limitation of the unit being used in

the process and to understand the operating parameters of the process concerning feedstock and other factors that may affect the process.

2.1.1. Temperature

Pyrolysis temperature has a great influence on the pyrolysis product of tyre decomposition. Waste tyre pyrolysis temperatures are between 400 and 500 °C. The product yield of the process (tyre pyrolysis oil, gas, and char) changes as temperature varies. It has been recorded that the low to medium temperature pyrolysis process favours the production of tyre pyrolysis oil while the high-temperature process favours the production of gases. Pyrolysis can be carried out through the fast or slow pyrolysis process. Fast pyrolysis is known for its high heating rate (1000 °C/s), short residence time of about 3 seconds and the fast quenching of the gaseous products. The characteristics of this process causes a minimal secondary reaction and in turn leads to a high pyro-oil yield.

In contrast, slow pyrolysis which are characterized by their low heating rate and long residence time promotes secondary reaction thus increasing the yield of gas and char products. Some examples of the effect of temperature under slow pyrolysis condition was investigated by Ramirez-Canon A et al., [10] who studied the degradation of the waste tyre at 450 to 600 °C and residence time of 90 min using hydrogen with a flow rate of 100 mL/min as the carrier gas. They recorded the highest oil yield of 37.25% at 550 °C and the lowest yield of 14.8% at 450 °C. The researchers also noted that a rise in temperature up to 550 °C resulted in a decrease in the sulphur content in the oil to 0.7%, while a further rise increased the sulphur content. In [31] the authors studied the pyrolysis of the waste tyre at a heating rate of 10 °C/min, N₂ flow rate of 100mL/min, the temperature range of 375–500 °C and noted the product yield at every 35 °C. At 425 °C, they recorded an increase in oil yield up to 60.02 wt%, which decreased to 54.1 wt% at 500 °C. The char yield also reduced from 50.67 wt% at 425 °C to 26.41 wt% at 450 °C and then remained constant throughout the process. A similar trend was confirmed by Kar [32], who studied the effect of the same temperature range (375–500 °C) and heating rate (10 °C/min). At 425 °C, a maximum yield of 60.0 wt% was obtained, which decreased to a yield of 54.12 wt% when the temperature was raised to 500 °C. The author attributed the decrease in yield to the occurrence of secondary reactions. An increase in the temperature also caused a decrease in the amount of char from 50.67 to 26.41 wt% whilst increasing the gas yield from 2.99 to 20.22 wt%. In comparison to diesel fuel, the crude tyre pyrolysis oil obtained when the temperature was between 450 and 650 °C, a heating rate of 5 °C/min, and residence time of 2 h had a higher viscosity and sulphur content [9].

Lopez et al. [33] pyrolyzed waste truck tyres employing flash pyrolysis. The pyrolysis process were carried out continuously for less than 30 min at a heating rate of 10 °C/min. The effect of temperature between 425–575 °C on the yield was studied. They noted that pyro-oil was the primary product formed (58 wt%) at 425 and 475 °C but reduced as the temperature increased to 575 °C. However, the gas yield increased linearly as the temperature increased while the char yield decreased in that trend. Another study on flash pyrolysis was carried out by Choi et al. [34], who pyrolyzed waste tyres at a temperature between 230–450 °C, the residence time of approximately 4 min, and heating rate of 5 °C/min. For each temperature, they recorded maximum yield in the oil product and less yield in the gas product due to the short residence time that limited secondary reaction from taking place. Although the temperature is the dominant parameter in pyrolysis, specific characteristics of the process such as heating rate, pressure, type of carrier gas, and the flow rate is also significant due to their direct

influence in the promotion of secondary reactions and, consequently in different yields of oil, gas, and char [35]. A future research recommendation would be to build a regression model that would predict product yield as functions of temperature, type of reactor, heating rate, tyre particle size, and any relevant parameter [36].

2.1.2. Heating rate

One of the earliest works in studying the effect of heating rate was carried out by Williams et al. [37]. They experimented with a stainless steel fixed bed reactor at temperatures from 300 to 720 °C with heating rates from 5 to 80 °C/min. They noted that at every final temperature, the oil yield increased with increasing heating rates. The highest oil yield of 58.8% was recorded at 720 °C and a heating rate of 80 °C/min. They explained that some of the hydrocarbon content of the char is volatilized by higher pyrolysis temperature. Uyumaz [29], using a stainless steel fixed bed reactor at temperatures between 400–500 °C with heating rates of 10, 15 and 20 °C/min observed that as the heating rate was increased, there was a corresponding decrease in the oil yield and grow in the gas yield. Maximum oil yield of 55% was attained at a heating rate of 10 °C/min at 450 °C. Rapid bonds breakage in the reactor due to an increase in the heating rate formed hydrocarbon molecules having a very low molecular weight that could not be condensed to a liquid. González et al. [38] also validated that higher heating rates induced more significant cracking of bonds, which resulted in higher gas yield. They used a stainless steel fixed bed reactor at a temperature of 600 °C and varied the heating rates from 5 to 20 K/min. At a heating rate of 15 K/min, the maximum oil yield of 55.4% was observed. Under atmospheric pressure, Banar et al. [39] studied a notable effect of heating rate, where an increase from 5 to 35 °C/min at a temperature of 400 °C produced gas and oil yield of 33.8 and 35.1 wt% respectively. It should be noted that different trends for oil yields with varying temperatures and heating rates have been recorded by various researchers. The inconsistencies can be attributed to underlying issues related to heat and mass transfer, causing the formation of different products, hence affecting the overall oil yield [35].

2.1.3. Particle size

In thermochemical processes, it is postulated that small particles present an isothermal behavior and have no limitation to internal mass transfer, while the opposite is the case for large particles [40]. Uniformity of temperature throughout the particle is the case for small particles, whereas, for larger particles, the interior of the particle heats up slowly. However, smaller particles are often accompanied by conversion to the liquid and gas phases. In contrast, for the larger particles, the interior remains in the solid phase due to the lower temperature [36]. Smaller particles are adequate if maximizing the oil yield is an important objective. For instance, Dai et al. [41], using a circulating fluidized bed reactor at 500 °C recorded a higher oil yield and a decrease in the char yield (from 45.0 to 30.0 wt%) when the waste tyre particle size was reduced from 0.8 to 0.32 mm. Similarly, the gas and liquid yield for 0.32 mm was recorded as 15.1% and 50%, respectively, which was higher than the particle size of 0.8 mm. The authors explained that the smaller particle size aids char reduction due to more reaction surface of the feedstock, which also led to more gas products.

Similarly, the effect of particle size ranging from 10–25 cm³ was studied by Aziz et al. [42]. They recorded an increase in the pyro oil from 40% at 10 cm³ to 42% at 15 cm³, which is the maximum, and

above this size, the oil yield began to reduce whilst an increase in the char yield. A lab-scale chemical vapour deposition reactor (CVD) with the temperature at 600 °C was used by Osayi et al. [43] to observe the influence of particle size on product yield. Particle size varying from 2–10 mm were pyrolyzed in the presence of nitrogen, as a carrier gas, of flow rate 150 mL/min, a reaction time of 30 min, and a heating rate of 15 °C/min. They recorded an increase in the oil yield from 24.5 to 34.4 wt% for a particle size of 2 and 6 mm, respectively. Beyond 6 mm, the oil yield was found to decrease progressively. Nevertheless, as the particle size increased from 2 to 10 mm, the gas yield steadily reduced as the solid residue increased. This is due to the low thermal conductivity and less exposed surface area of the feedstock.

2.1.4. Reactor type

The type and configuration of reactors also influence the products of waste tyre pyrolysis. Reactors like autoclave, entrained bed, kiln, rotating cone, auger type, fluidized bed, fixed bed, spouted bed, vacuum pyrolyzer, free fall, vortex type, plasma type, and ablative type have been studied [44,45]. Helleur et al. [46] carried out ultra-fast waste tyre pyrolysis by employing the use of an ablative reactor at 550 °C and under N₂ atmosphere. Ablative pyrolysis is associated with fast or flash pyrolysis where heat is transferred directly between the rotating or heated disc and the feedstock. This feedstock is compressed between the cold stationary element and the hot rotating one. To prevent condensation reactions and secondary polymerizations, the reactor was designed to reach the desired temperature within one second. Complete decomposition of the used tyre was achieved, and primary products were recovered. The recovered carbon black (ash content of 15.2%) was observed to be useful in rubber compounding but cannot be employed in recycling for tyre manufacturing. After activation, it was noted that the ash content dropped. This was attributed to the removal of unknown organometallic compounds from the char. The activated char was successfully applied in the removal of organics from aqueous solutions [46]. Black and Brown [47] used a continuous ablative reactor having a capacity of 5–20 kg/h to carry out ablative pyrolysis on waste tyres. The feedstock was manually loaded into the hopper and transported to the reactor by a discharge screw at variable speed. The reactor system was externally heated to 550 °C in six independently controlled zones, and there was continuous contact between the metal surfaces and the feedstock particles. The solid phase was separated in the cyclone and the produced vapours were condensed in a three-stage fractionating unit followed by a water-cooled heat exchanger while the non-condensable gases were filtered to remove oil droplets before analysis. They recorded a yield of 49.6 wt%, 16.9 wt% and 33.5 wt% for the liquid, gas and char products.

Fixed bed reactors, which are very simple in design and operation, are the most used in the pyrolysis of waste tyres, especially in laboratory and bench-scale units. However, due to the low heat transfer rate of this reactor, difficulties in continuous operation, and scale-up, there's limited economic interest for full-scale applications of the fixed bed reactor. A laboratory-scale fixed bed with a cylindrical reactor having a diameter of 0.19 m and a height of 0.24 m was used to pyrolyze waste truck tyres by Akkouche et al. [48]. At the top of the heating zone, the reactor had a tube for discharging gaseous products into a water cooler to condense it to liquid. The researchers also noted the influence of the heating rate on product yield. They observed a higher yield of gas and a significant amount of hydrogen in the gas when the heating rate was high. However, the oil yield was decreased, possibly due to the prolonged time the pyrolysis products spent in the reactor, in which the gaseous

products flowed through a centrally placed steel column.

Similarly, Mkhize et al. [49] analyzed the influence of the final temperature (350–550 °C) and heating rate (5–25 °C/min) in the batch pyrolysis in a fixed bed slow pyrolysis reactor of length 0.85 m and diameter of 0.06 m. The reactor was purged with a 99.9% pure nitrogen gas at a constant flow rate of 1 L/min and loaded with 40 g of waste tyre feedstock. Gaseous products from the reactor was passed through a series of five vertically placed condensers cooled with dry ice at –10 °C to condense the oil while the non-condensable gases were vented to the atmosphere. The experiments conducted in this reactor indicated a significant effect of the temperature on oil yield and an insignificant impact of the heating rate. However, the effect of both the pyrolysis temperature and the heating rate was significant for limonene production.

Aziz et al. [42] also carried out the analysis using a fixed bed reactor (height: 990 mm, diameter: 480 mm) which was made of stainless steel, having a feeder header (height: 80 mm, diameter: 120 mm) at the top and an exit (diameter: 200 mm) for char removal at the bottom of the reactor. Two hexagonal stainless steel pipes were placed inside the reactor to aid uniform heating supplied by a fuel burner. Two vertical condensers of length 1520 mm and diameter 170 mm were connected at the top of the reactor to capture condensed gas from the reactor, which was done by passing cold water through the condensers. The temperature of the process was varied at 300–500 °C. They recorded a high oil yield of 42 wt% at a temperature of 400 °C and feed size of 15 cm³. The researchers concluded that the high viscosity value (4.5 centistokes) and heating value (42.5 MJ/kg) makes the pyro-oil unsuitable for direct use in engine operations but as furnace oil or fuel in boiler operations.

In another study, Cunliffe and Williams [50] pyrolysed 3 kg of waste tyre in a fixed bed batch reactor of height 0.36 m and diameter 0.24 m. The reactor was electrically heated at temperatures between 450–600 °C. The nitrogen gas was passed through a perforated ring at the top of the reactor after undergoing preheating. Products from the process were passed through two water-cooled condensers to separate the liquid and gaseous phase for analysis. Ucar et al. [51] experimented with a fixed bed stainless steel vertical reactor. The laboratory scale, the semi-batch reactor, had a diameter and height of 0.06 and 0.21 m, respectively. The reactor containing 130 g of waste tyre feedstock was heated by an electric furnace to temperatures of 550, 650 and 800 °C in a nitrogen atmosphere. Products from this process were passed through four traps: two ice baths and two containing lead nitrate solution for hydrogen sulphide capture. The amount of the captured hydrogen sulphide was obtained by filtering, rinsing and drying the lead sulphide. Tedlar bags were used to collect the remaining gas for analysis.

Another pyrolysis technology for fast pyrolysis conditions is the fluidized bed reactors, which enhances oil yield and supports continuous operation, which is relevant for the scale-up of the process. Nevertheless, the complex design and operation of this system, coupled with the high investment needed to run this reactor, limits the utilization of the fluidized bed reactors [52]. Raj et al. [53] conducted research using a multi-variant experimental approach in waste tyre pyrolysis to maximize oil yield and reduce gas and char output. The stainless steel fluidized bed reactor having an internal diameter of 50 mm was loaded with sand to a height of 0.3 m supported on the perforated base to enable fluidization of the tyre and was electrically heated at a rate from 700 to 1100 K/s. The waste tyre particles stored in the hopper was fed into the reactor employing a screw feeder having a variable speed motor to regulate the feed rate. Before feeding these waste tyre particles, the reactor was first flushed with compressed air to obtain a uniform temperature in the bed, after which the air was replaced with

nitrogen to prevent combustion and oxidation. In carrying out the pyrolysis experiment, the temperature of the range 350–600 °C, particle size (0.3–1.18 mm), and feed rate (0.78–1.50 kg/h) were the process parameters employed. They also studied the influence of these process parameters for each response model (oil, gas, and char yield) with the aid of analysis of variance (ANOVA). They recorded optimal parameters of 475 °C, 0.74 mm, and 1.05 kg/h, which gave optimum yields of oil (40.8 wt%), gas (31.4 wt%), and char (31.0 wt%) [53].

Dai et al. [41] studied the continuous pyrolysis of waste tyres in a circulating fluidized bed reactor using quartz sand as the circulating fluidizing agent. Their study focused on the influence of temperature (360–810 °C) and gas residence time (1–5 s) on the pyrolysis process. The fluidized bed consisted of five parts: combustion chamber, variable speed screw feeder, reactor assembly with two cyclones, cooling system, and a gas circulating pump. The K-type (chromel–alumel) thermocouples were used in measuring the temperature profile along the reactor and at the gas exit point. The tyre powder undergoes fast pyrolysis and instantly removed from the CFB while the quartz sand and residue char are separated by two cyclones and the produced vapour sent to the condensation system where it is collected and analysed. Mkhize et al. [54] recently published a study comparing the influence of residence time and heating rate on product yields and composition of a bubbling fluidized bed reactor (BFBR) with that of a fixed bed and a conical spouted bed. The BFBR was made up of the feeding system, the reactor, and the char separation system. A hot cylindrical chamber having eight 6.6 kW heating elements was used in heating the reactor. The reactor and the fluidizing nitrogen gas were preheated at 475 °C before the start of the process to ensure rapid pyrolysis. Lastly, the products were introduced into the condensation system consisting of two water-cooled (temperature of 5 °C) tube-and-shell condensers made of stainless steel. The oil product was collected for further analysis.

Rotary kiln reactors are of great interest due to their simple design and construction. Also, the residence time of the solid can be easily adjusted, has good heat transfer during slow rotation, and there's the possibility of continuous operation. However, the low heat efficiency is the major limitation of this type of reactor [55]. A pilot-scale continuous rotary kiln reactor was used in the pyrolysis of the waste tyre at temperatures between 450 and 650 °C and pressure between –20 to –10 pascal [56]. It consisted of a pyrolytic rotary kiln main reactor and peripheral systems, including a supply system, a condenser and reservoir, a demister filter, a solid residue collection tank, a gas burner, a flue gas cleaner, and an effluent gas sampling system. The diameter and length of the kiln were 0.3 and 3.0 m, respectively. The total power of 30 kW supplied by three individual PID controlled heaters was used in the heating of the reactor. Under these conditions, the maximum oil yield of 45.1 wt% was recorded at 500 °C. Gas and char yield at this temperature were 13.6 and 41.3 wt%, respectively. The authors compared these values with that of Murillo et al. [31], who used a similar rotary kiln reactor and obtained a maximum oil yield of 53.0 wt% at 500 °C. They explained that this could be due to the more considerable length of the kiln to diameter ratio (8 m) used in their study. The larger the length to diameter ratio, the higher the residence time of the vapour hence a reduction in pyro-oil yield. After analysis, they concluded that the pyrolytic oil could be used as liquid fuel due to their high heating value (40–42 MJ/kg), excellent viscosity (1.6–3.7 centistokes), and minimal sulphur content of 0.97–1.54 wt%. The char, which was activated using carbon dioxide, was said to have the capability for use as adsorbents of relatively large molecular species. The non-condensable gases were passed to the burner after the removal of acids in the scrubbing unit.

Spouted beds reactors have similar characteristics as the fluidized bed reactors such as bed isothermic, high heat transfer rate, and good solid mixing with gas-solid contact. However, a

significant difference between the two is the ability of the former to entertain whole, coarse, and irregular tyre particles without grinding, thereby having a great influence on the economy of the overall process. Also, the gas residence time in the spouted bed is shorter than that in the fluidized bed while a higher heat and mass transfer rate is noted. This short residence time limits the occurrence of secondary reaction in the gas phase leading to an increase in the oil yield and allows for operations under fast pyrolysis conditions. Furthermore, the cyclic particle movement in the spouted bed prevents bed defluidization by particle agglomeration and local overheating. It inhibits heat transfer between phases, which is vital for the treatment of a low conductivity material such as rubber [52,55]. Initially, the product distribution from the pyrolysis of waste tyres was studied in a batch regime in a bench-scale unit provided with a conical spouted bed reactor [57]. A subsequent study by Alvarez et al. [58] analyzed the effect of temperature on the properties of pyro-oil from the fast pyrolysis of waste tyre in a conical spouted bed reactor. The reactor consisted of a solid and gas feeding device, high efficiency cyclone, a double shell tube condenser where the liquid product was collected, and the gaseous product analysis system. Nitrogen was used as the fluidizing agent. The CSBR was heated by two independent sections radiant oven, and the pyrolysis temperature was measured using two K-type thermocouples located inside the reactor (at the bed annulus and close to the wall). The gases leaving the condensation system were filtered with two coalescence filters before analysis.

The auger reactor is a promising pyrolysis technology that allows operating from fast to slow pyrolysis. This reactor is known for its simple design, ease of operation, and low energy input. Besides, little or no carrier gas is required when operating this reactor, and the operating parameters can be controlled with ease to obtain the desired products. Using a continuous pilot-scale auger reactor with processing and nominal capacity of 15 kg/h and 150 kWth respectively, Martínez et al. [59] pyrolyzed waste tyres of particle size between 2 and 4 mm. The process was which was operated at 550 °C, 1 bar, and nitrogen gas as inert generated reaction enthalpy of around 907.1 kJ/kg. The residence time of 3 min was fixed by adjusting the rotation speed of the screw inside the reactor. Under these conditions, the solid, liquid, and gas yield obtained were 40.5, 42.6 and 16.9 wt%, respectively. The combustion of the gas fraction at 900 °C led to the generation of 4200 kW of power for the flue gas. They proposed that this gas fraction could be used to supply the energy needed for the pyrolysis process (which is about 1000 kW) as well as for other thermal applications and power generation. The mass balance closure carried out on the process showed excellent credibility of the data coupled with the excellent reproducibility and stability of the reactor hence the possibility of a scale-up.

Recently, there has been growing interest in the microwave pyrolyser. This could be due to its enhanced heat transfer and its operation under isothermal conditions in the reactor. Also, microwave heating is suitable for materials with low heat conductivities and improves control over the pyrolysis products. Also, the generated carbon black is an excellent microwave adsorbent and can be regarded as an internal heat source [52]. One of the earliest works on microwave pyrolysis of the waste tyre was performed by Undri et al. [60]. They investigated the effect of microwave power (P) and sample mass (M) on the pyrolysis of waste tyres and adopted P/M^2 as a new descriptive parameter because it gave a bright and concise correlation among experimental conditions and results of the pyrolysis test. Subsequently, they also studied the properties of pyrolytic oils and char gotten from microwave pyrolysis [61–64]. However, their focus was on the effect of different factors on the pyrolysis products as against the yield and composition of the products at various stages during the microwave pyrolysis. Therefore, studying the evolution of the pyrolytic products is essential in learning about the design and mechanism of the microwave pyrolysis of the waste tyre as investigated by Song et al. [65] using a lab

scale microwave oven. The temperature profiles, product yields, and composition at various stages were the parameters studied in this research. The microwave oven had a power intensity range of 0–900 W at a frequency of 2.45 GHz and was operated continuously. They observed a fast rise in temperature during the process and inferred that this could be a result of the violent absorption of carbon black and other possible materials (e.g., iron) in the tyre thus heating the sample quickly and triggering the intense pyrolysis.

From the recorded studies above, it can be concluded that the type and configuration of reactors affect the decomposition of waste tyres. However, during the selection of the reactors, factors such as economics, desired products, available resources, nature of feedstock, and so on should also be taken into consideration.

Different types of waste tyres have been thermally pyrolyzed, including passenger vehicle tyre [66], heavy vehicle tyre [67], and bicycle tyre [28]. The major compounds of the liquid oil comprise of heavy crude with large carbon chains [44]. Besides, the low octane number of liquid fuel and the presence of high solid residues and impurities such as sulphur characterizes it as a low-quality oil [4]. Various conditions affect the yield of each pyrolysis product. These conditions are temperature, pressure, heating rate, feed particle sizes, catalysis, the configuration of the reactor, and type and flow rate of inert carrier gas. Table 1 gives a summary of the research done on non-catalytic pyrolysis, the operating conditions, and the fraction yield.

3. Cons and limitations of the non-catalytic pyrolysis

The production of liquid oil, gas, and char is the main focus of thermal pyrolysis. The oil could serve as a fuel or as feedstock for various chemical processes. The pyrolysis gases, predominantly consisting of C₁–C₄ hydrocarbons and hydrogen, have a high calorific value, which makes it a good source of heat for the process [68]. However, the liquid oil is of low quality due to the presence of high solid residues and impurities such as sulphur, nitrogen, and phosphorus [40]. The oil is also characterized by its high activation energy and high boiling point range [20]. Furthermore, high reaction temperatures (350–900 °C), longer residence time, and the low thermal conductivity of the feedstock make it a high energy-intensive process [2, 69].

4. Catalytic pyrolysis

The catalytic pyrolysis, which is carried out in the presence of a catalyst, has become a significant area of investigation for waste tyre pyrolysis. It is often characterized by its ability to increase gas yield while decreasing liquid yield by effectively cracking hydrocarbons into shorter chain lengths. The use of catalysts in tyre pyrolysis also influences the pyrolysis rate, quality, quantity yields of products, and composition such as aromatics for chemical production [70]. Although microporous acid zeolites have been the most studied catalysts, other ones such as mesoporous acid materials and basic catalysts have received attention in the literature. Examples of catalysts used in tyre pyrolysis include CaC₂, MgO, ZSM-5, USY, Cu/HBETA, MgCl₂, Ca(OH)₂, and so on. Operating conditions influence product distribution and composition for different catalysts. Table 2 gives a summary of some catalytic pyrolysis processes, the operating parameters, catalysts used, and their corresponding product yield. The effect of these catalysts on the product yield, oil composition, oil quality, its physical properties and its influence on the gas and char products are reviewed in the next sections.

Table 1. Summary of tyre pyrolysis conditions for oil production.

Tyre characteristics	Type of reactor	Operating parameters							Yield %			Reference
		Tyre size	Temperature range (°C)	Optimum temperature (°C)	Reaction time (min)	Heating rate (°C/min)	Mass of sample (kg)	Inert gas; flowrate (mL/min)	Oil	Gas	Char	
Steel free tyre samples	Fixed bed reactor	1–4 mm	350–600	400	60	5 35	0.01	n.r	38.8 31.1	27.2 33.8	34.0 35.1	[39]
n.r	Circulating fluidized bed reactor	0.32 mm 0.8 mm	360–810	500	n.r	n.r	5	Air	50.0 40.1	15.1 10.0	30.0 45.0	[41]
Bus tyre	Fixed bed reactor	10 cm ³ 15 cm ³ 20 cm ³ 25 cm ³	300–500	400	180	n.r	20	N ₂	40.0 42.0 38.0 31.0	11.0 14.0 19.0 20.0	49.0 44.0 44.0 48.0	[42]
Steel free tyre samples	Stainless steel batch reactor	1–1.4 mm	450–600	550	90	n.r	0.12	H ₂ ; 6.5	37.25	30.5	30.0	[10]
Bus tyre	Fixed bed reactor	0.75 cm ³ 2.25 cm ³ 1.25 cm ³	300–600	450	n.r	n.r	1.5	N ₂	42.0 38.0 40.0	10.0 11.0 13.0	45.0 50.0 49.0	[52]
n.r	Lab-scale CVD reactor	2 mm 4 mm 6 mm 8 mm 10 mm	375–750	600	30	15	0.1	N ₂ ; 150	24.5 27.01 34.4 31.5 29.2	42.5 20.5 16.3 15.0 13.1	33.0 49.2 48.5 48.7 53.6	[43]
Scrap passenger vehicle	Lab-scale pyrolyser	n.r	300–600	550	n.r	20	0.52	N ₂	40.0	-	-	[66]
LVT*	Batch pyrolysis reactor	1–3 cm	550–800	650	n.r	20	0.2	N ₂ ; 100	51.0	9.1	40.0	[67]
MVT*				750					45.5	12.5	42.3	
HVT*				750					63.5	10.0	28.5	
n.r	Fixed bed reactor	0.85–1.6 mm	400–500	450	20	10 15 20	0.05	N ₂ ; 1000	53.3 45.2 42.0	9.0 20.4 20.4	39.0 38.0 37.5	[29]
n.r	Fixed bed reactor	30–50 mesh	350–450	350 400 450	240	13	0.5	N ₂	53.2 62.8 57.2	3.1 11.2 17.3	43.7 26.0 25.5	[53]
Trucks	Fixed bed reactor	10 mm 15 mm 20 mm	350–550	550	50	10	0.03	N ₂ ; 1000	47.0 38.0 42.1	-	-	[27]
n.r	Pilot scale continuous auger reactor	2–4 mm	550	550	30		560	N ₂ ; 150	42.6	16.9	40.5	[44]

n.r: not recorded; *LVT: Light vehicle tyre; *MVT: Medium vehicle tyre; *HVT: Heavy vehicle tyre.

Table 2. Summary of typical catalytic pyrolysis conditions, catalyst characteristics and fraction yield.

Catalyst type	Catalyst characteristics	Quantity/ratio	Operating parameters					Yield %				Reference
			Tyre size	Temperature range (°C)	Reaction time (min)	Heating rate (°C/min)	Inert gas; flowrate (mL/min)	Oil	Gas	Char	Coke	
ZSM-5 Al ₂ O ₃ CaCO ₃ MgO	n.r	n.r	6 mm	450–500	55–65	11	N ₂	30.0	25.5	44.8	-	[14]
Regenerated NiMoS/Al ₂ O ₃	S _{BET} : 198.75 m ² /g; Pore volume: 0.42 cm ³ /g; Pore width: 8.86 Å		8–18 mesh	500	90	10	N ₂	33.1	21.2	40.0	8.0	[71]
Y-Zeolite	Pore size: 7.8 Å; Si/Al ratio: 5.4	Catalyst/tyre ratio of 1:1	1–1.4 mm	430–600	60	10	N ₂	32.2	21.8	38.0	8.0	[72]
ZSM-5	Pore size: 5.6 Å; Si/Al ratio: 40							34.6	20.0	38.0	7.6	
HY/MCM-41 core shell composite	S _{BET} : 790 m ² /g; pore volume: 0.85 cm ³ /g; pore size: 29 nm	Mass of catalyst: 7.5 g	20–40 mesh	350–500	120	n.r	N ₂ ; 30	42.0	9.1	41.2	4.3	[73]
ZSM-5	n.r	CT ratio 0.1	0.75 cm ³	300–600	n.r	n.r	N ₂	35.83	12.1	47.1	-	[74]
MgO	n.r	CT ratio 0.15	5–10 mm	300–400	120	n.r	n.r	35.63	15.2	49.7	-	[74]
CaCO ₃	n.r	n.r	5–10 mm	300–400	120	n.r	n.r	39.8	24.4	35.8	-	[13]
Na ₂ CO ₃	n.r	10% catalyst	n.r	400–600	45	n.r	n.r	32.23	32.53	35.23	-	[75]
Cu/HBETA	S _{BET} : 413 m ² /g; pore volume: 0.200 cm ³ /g	Mass of tyre: 30 g; Mass of catalyst: 7.5 g	20–40 mesh	350–500	90	10	N ₂ ; 30	49.2	-	-	-	[16]
Cu/HY	S _{BET} : 488 m ² /g; pore volume: 0.256 cm ³ /g							39.0	11.0	40.5	7.1	
Cu/HMOR	S _{BET} : 345 m ² /g; pore volume: 0.180 cm ³ /g							40.1	12.0	40.5	5.0	
								41.0	11.1	41.0	4.0	

Continued on next page

Catalyst type	Catalyst characteristics	Quantity/ratio	Operating parameters					Yield %				Reference
			Tyre size	Temperature range (°C)	Reaction time (min)	Heating rate (°C/min)	Inert gas; flowrate (mL/min)	Oil	Gas	Char	Coke	
ZSM-5	Si/Al ratio: 30; S _{BET} : 541 m ² /g; pore size: 5.6 Å	Mass of tyre: 150 g; mass of catalyst: 1.5 g	20–100 mesh	500	30	15	N ₂ ; 400	55.65	6.49	37.86	-	[15]
USY	Si/Al ratio: 5.4; S _{BET} : 432.5 m ² /g; pore size: 7.8 Å							53.49	9.97	36.54		
B	Si/Al ratio: 73; S _{BET} : 524 m ² /g; pore size: 6.5 Å							54.00	8.24	37.76		
ZSM-22	Si/Al ratio: 58; S _{BET} : 350 m ² /g; pore size: 5.6 Å							55.12	10.45	34.43		
SAPO-11	Si/Al ratio: 4; S _{BET} : 186 m ² /g; pore size: 6.7 Å							55.12	6.17	38.71		
Fe/HMOR	S _{BET} : 352 m ² /g; pore volume: 0.176 cm ³ /g; pore width: 6.50 Å	Waste tyre/catalyst ratio: 4	-	350–500	120	10	N ₂ ; 30	41.05	13.5	40.7	2.01	[76]
Fe/HBETA	S _{BET} : 406 m ² /g; pore volume: 0.234 cm ³ /g; pore width: 6.59 Å		42.23	12.1	40.7	4.51						
Fe/KL	S _{BET} : 98.8 m ² /g; pore volume: 0.047 cm ³ /g; pore width: 6.62 Å		42.0	13.0	41.5	2.41						
Fe/HZSM-5	S _{BET} : 265 m ² /g; pore volume: 0.131 cm ³ /g; pore width: 6.82 Å		39.51	18.6	40.5	3.0						

n.r.: not recorded; SBET: surface area.

4.1. Effect of catalyst on product yield

As previously stated, the addition of catalysts in the process aids in the increase of gas products while decreasing the oil and char yield. Different operating parameters such as heating rate, particle size, feedstock composition, pyrolysis time, type, and design of reactor affect the product yields and properties. Various researches have been carried out with different catalysts and operating parameters to analyze the output of pyrolysis products. Hossain et al. [74] noted that the catalyst tyre ratio influences the yield of pyrolysis products. They investigated the effect of catalyst tyre ratio of 0.1 and 0.15 on pyrolysis of the waste tyre using the ZSM-5 zeolite at an optimum temperature of 460 °C. They recorded that as catalyst ratio and temperature increased, char and oil production increased while gas yield decreased. The predominant properties of ZSM-5 zeolite, including its acidity adjustability, hydrothermal stability, and flexibility, make it a suitable catalyst for catalytic pyrolysis [77]. Kordoghli et al. [14] studied the influence of acid (ZSM-5 and Al₂O₃) and base (CaCO₃ and MgO) powdered catalysts on oil yield. Using a fixed-bed reactor, the temperature of 550 °C, and mode of catalysis as in situ method, they recorded the highest conversion at 63.1% and 62.5% with CaCO₃ and Al₂O₃ catalysts, respectively. They concluded that CaCO₃ and Al₂O₃ are the most suitable catalysts for increasing the gas yield, while the MgO favours the formation of liquid output.

While comparing the liquid yield between thermal and catalytic pyrolysis using five various zeolite catalysts at 500 °C, Li [15] observed a limited effect of the catalyst on oil yield. However, the gas yield increased, and that of char decreased significantly. The gas yield rose to 6.17–10.45 wt%, which was twice that of thermal pyrolysis, the char yield fell to 34.43–38.71 wt%, and no notable change was observed for the liquid yield. Iron metal, known for its hydrogenation and ring-opening reactions activities, was used as support on zeolites for the pyrolysis of waste tyre by Muenpol and Jitkarnka [76] to ascertain its effect on the process. From the results, it was deduced that cracking ability of the products improved by the addition of 5% Fe on the zeolites. This was seen in the increase of the gas yield as the liquid yield decreased.

Furthermore, the heavier gases reduced while light hydrocarbon gases increased accordingly. Further study on the effect of catalyst pore size on liquid yield was done by Boxiong et al. [78]. They pyrolyzed waste tyre in a two-stage fixed-bed reactor at a temperature from 300–500 °C using zeolite USY and ZSM-5 catalyst with pore size 9.0 and 5.6 Å, respectively. The liquid yield with USY catalyst (32.6 wt%) was observed to be less than that with the ZSM-5 catalyst (40.4 wt%). They explained that large sizes of hydrocarbon quickly passed through the pore system of the USY catalyst due to its larger pore size of 9.0 Å thus producing lighter hydrocarbon molecules.

Fahed [79] compared the results of oil yield from thermal and catalytic pyrolysis under operating conditions of temperature at 550 °C, heating rate of 150 °C/min, and the activated alumina and zeolite Jo as catalysts. They recorded a maximum oil yield of 49.32% and 51.54% for activated alumina and zeolite Jo catalysts, respectively. ITQ-21 and ITQ-24 zeolites were also mixed with HMOR zeolite catalyst in tyre pyrolysis. With the pure HMOR catalyst, a yield of 40.3% was recorded. The addition of 2% ITQ-21 and ITQ-24 increased the liquid oil yields to 41.0% and 42.4%, respectively [80].

Saeng-arayakul and Jitkarnka [71] used a spent NiMoS/Al₂O₃ catalyst from a hydrodesulphurization unit. The catalyst having a surface area of 198.75 m²/g and pore volume

of 0.42 cm³/g was placed above the feed allowing contact with only the vapour from the pyrolysis process. They recorded a decrease in the oil yield from 42 to 32 wt% with a corresponding increase in the gas yield (from 19.5 to 21.3%) and coke formation while the solid yield remained constant. This increase in gaseous products indicates the high reaction activity of the catalyst.

An increase in the gas yield from the use of acid catalysts, as stated above, is not always the case as shown by Shah et al. [12], who investigated the effect of temperature, time, and amount of catalyst on the product yields using carbon-based, carbon carbide (CaC₂) catalyst. At the optimum temperature of 350 °C, the influence of the catalyst/feed ratio of 0.1 to 0.5 was investigated. The result showed an increase in liquid oil up to 38.4% when the catalyst/feed ratio of 0.2 was used while char and gas decreased to 32% and 29.6%, respectively. The higher oil yield was ascribed to the presence of pi electrons in CaC₂. They explained that the vibration of these pi electrons enhanced the vibrational energy of the tyres up to resonance and hence forms polymer radicals.

It can be concluded that for the most catalytic process, the impact of catalyst favours the gas yield while reducing the amount of oil yield, thus increasing the light oil fraction with no significant change in char yield. From the literature, it can be deduced that catalytic pyrolysis comprises of two stages. In the first stage, the waste tyre is liquefied at a low temperature to obtain a mixture of liquid hydrocarbons and solid carbon black with a decomposition of components with a lower boiling point. At the next stage, an increase in the reaction temperature causes the liquid hydrocarbons from the first stage to come in contact with the active sites of the catalyst, thus reacting quickly and shortening the reaction time. Consequently, the condensation of coke on the surfaces of carbon black takes place, and the catalyst is inhibited.

4.2. Effect of catalyst on oil quality

The oil derived from catalytic pyrolysis is characterized by its brownish colour, low viscosity, and good fluidity. This indicates that the oil has a relatively high content of light fraction [15]. The sulphur content and energy yield (heat value) are two parameters used to describe the adequacy of pyro-oil to be used as a fuel. The high sulphur content of the oil is a significant factor limiting its use as a direct fuel. Vulcanization agents and accelerators such as benzothiazole, 2-mercaptobenzothiazole used in the production of tyres are the major sources of sulphur in the pyro-oil [76]. Therefore, catalytic reforming is broadly used to expand the significant chemical compounds, lessen the sulphur content, and upgrade the oil quality. Broad examinations about rubber waste by catalytic pyrolysis overhauling have been led by numerous specialists utilizing metal oxides, metal/zeolite catalysts, base catalysts, mesoporous and microporous zeolites [81].

Namchot and Jitkarnka [82] synthesized a 5 wt% Ni/ZSM-5 catalyst. They found that the fuse of Ni reduced sulphur content in pyrolytic oil by 29.2 wt% for the most part by thwarting the development of benzothiophenes, dibenzothiophenes and naphthothiophene. Yuwapornpanit and Jitkarnka [16] also altered Hb, HY and HMOR zeolites with 5 wt% Cu to pyrolyse waste tyre in pyrolysis reactor with two stages, the pyrolysis zone maintained at 500 °C and the catalytic zone at 350 °C and found that the copper-altered catalysts can generate less sulphur in the pyrolytic oil than their relating zeolites by converting sulfur-containing compounds into similarly synthetically stable structures. In this manner, it may be inferred that metals adjusted zeolites can upgrade the nature of the pyrolytic oil by halfway evacuating the sulphur. The reduction of sulphur by a metal/zeolite catalyst was also observed by Muenpol and Jitkarnka [76], who studied the effect of Ni

and Fe doped catalyst oil quality. They observed a reduction of the sulphur content and a significant increase in the aromatic formation.

It was proven that the spent NiMoS/Al₂O₃ catalyst is suitable for sulphur removal in the pyrolysis product. In the non-catalytic oil, a significantly high amount of sulphur was recorded which reduced from 1.36 to 0.60 wt% in the presence of the NiMoS/Al₂O₃ catalyst, thereby resulting in a high deposition of sulphur in the form of H₂S on the spent catalyst. They reasoned that the catalyst had the capacity in both cracking and desulphurization concurrently [71]. Similarly, a low concentration of sulphur was recorded by Ayanoglu and Yumrutas, [83] after the catalytic pyrolysis of waste tyre with CaO catalyst. The sulphur content in the thermal pyrolysis was recorded as 1.42 wt%, which reduced significantly to 0.8 wt% after CaO was used. Seng-eiad and Jitkarnka [84] studied the potency of untreated and HNO₃-treated chars in the removal of sulphur from pyro-oil. The char was obtained from the thermal pyrolysis of waste tyres. They noted a significant decrease in the concentration of sulphur of about 26.6–27.3% was recorded for both the untreated and the treated char. However, the sulphur compounds (benzothiazoles, thiophenes and benzothiophenes) found in the pyro-oils were different due to the differences in pore size, acidity and surface area of the catalysts. However, when İlkılıç and Aydın [4] carried out motor test utilizing catalytic oil with decreased sulphur content (approximately 0.9%), the fumes discharge results indicated that CO, unburned hydrocarbons, SO₂ and smoke obscenity were all higher than diesel-burning, with CO, SO₂ and hydrocarbons reaching levels multiple times higher than diesel emanations at certain motor speed. They believed that the primary reasons behind higher hydrocarbon and CO emissions for the oil were poor atomization, lower cetane number, and prolonged start delays.

4.3. Effect of catalyst on pyro-oil composition

High carbon chain compounds in the range C₅ to C₂₆ are the prevalent products in the oil of thermal pyrolysis of waste tyres. However, in the presence of a catalyst, the heavy oil is broken down into smaller gas fractions (C₅–C₁₂) [80]. The composition of the pyro-oil acquired from waste tyre catalytic pyrolysis have been examined by some researchers. Most recorded works have attributed the increase of single-ring aromatic compounds in the oil to the presence of zeolite-based catalysts. Wang [85] explored the influence of 4 zeolite catalyst types (USY, HY, HBeta, and silicoaluminophosphate (SAPO)) on the structure and distribution of aromatic hydrocarbons in the fast catalytic pyrolysis of waste tyres. Aromatic hydrocarbons, the predominant compound, was one of the products of the pyrolytic oil followed by alkenes and alkanes. It was recorded that the USY catalyst had the best catalytic performance, which was merited to its high surface area (734 m²/g), large pore volume (0.33 cm³/g), and high content of strong acid sites (1.21 mmol/g). These characteristics of the USY catalyst improved hydrogen transfer and led to the catalytic reforming process towards the formation of more aromatic hydrocarbons. In another study by Miguel et al. [86], the presence of the HZSM-5 catalyst, improved the concentrations of benzene, toluene, and xylene from 0.21 to 3.64 wt%, 0.78 to 7.39 wt%, and 1.23 to 9.00 wt%, respectively while causing a reduction in the olefinic hydrocarbons. This was not the case for the HY catalyst, which showed only a small increase in these compounds. However, the HY catalyst increased the polyaromatic compounds significantly when compared with the HZSM-5 catalyst. Polyaromatic compounds such as naphthalene, methyl-, dimethyl- and trimethyl naphthalenes increased from 0.24 to 4.95 wt% and

from 0.22 to 11.9 wt% respectively. The increase in the polyaromatic hydrocarbon content is said to be as a result of Diels–Alder dehydrogenation of alkanes to alkenes accompanied by cyclization and aromatization, which are accelerated by the steric and acidic properties of the catalysts [86]. From various studies in literature, it was observed that zeolites, especially HZSM-5 and HY, increased the concentration of benzene, toluene, xylene (BTX) with the HY zeolite having larger pores and stronger acid sites, which enhanced the formation of monoaromatic hydrocarbons. In general, large pore sizes of the catalysts would allow the entrance of large molecular size hydrocarbons into their pores, thereby leading to catalytic cracking of the hydrocarbons to form aromatic hydrocarbons [15,19,72,78,87,88]. Another factor that influences the aromatic content in the pyro-oil is the Si/Al ratio of the zeolite. Low Si/Al ratio in the HY zeolites enhances the activity of the process, which in turn increases the aromatic hydrocarbon content; however, coke formation is increased [89]. Olazar et al. [90] used a conical spouted bed reactor also to investigate the influence of HY and HZSM-5 zeolite catalysts on oil composition. The addition of the catalysts raised the concentration of single-ring aromatic compounds from 20.17 wt% (without catalyst) to 32.49 wt% for the HZSM-5 and 40.49 wt% for the HY catalyst.

Furthermore, a higher concentration of BTX was recorded in the presence of the catalysts as compared to thermal pyrolysis. However, the concentration of polyaromatic hydrocarbons such as naphthalene increased in the presence of the HY catalyst and was insignificant with the HZSM-5 catalyst. The compositions of catalyzed and uncatalyzed pyrolysis oil for the yield of higher value aromatic hydrocarbons was analyzed by Williams and Brindle [72]. The single ring aromatic concentrations in the uncatalyzed tyre pyrolysis oils were found to be low in strength, hence the inability to extract useful chemicals from the oil. Nevertheless, in the presence of the Y zeolite (CBV-400) and zeolite ZSM-5 catalysts, a significant rise in the concentration of aromatic hydrocarbons, especially benzene, toluene, and xylenes was noted. The Y zeolite (CBV-400), having larger pore size and surface activity was recorded to have produced higher aromatic content of 44.7 wt% as against a content of 2.8 wt% from the uncatalyzed process in the product oils.

Other types of zeolites such as the HBeta, HMOR, and SAPO-11 have also been used to improve the quality of pyro-oil in catalytic pyrolysis. Dũng et al. [91] showed that in the presence of HMOR and HBeta catalysts, polar aromatics reduced by 30% and 50%, respectively. The strong acid sites, smaller crystalline, and large sinusoidal pore system of the HBeta catalyst are the underlying factors for its better cracking activity than the HMOR catalyst. H β , HZSM-22, SAPO-11, ZSM-5, and USY zeolites were used to study their influence on pyro-oil by Li et al. [92], and they recorded the lowest content of single-ring aromatics (39%) and the highest aliphatic contents (57%) in the oil from HZSM-22 catalyst. This was due to the low acidity and small pore size of the catalyst, which resulted in very low activity. However, the high acidity and larger pores of the H β and SAPO-11 catalysts gave the highest contents of alkyl-benzenes.

The use of iron-modified zeolites, the olefins and naphthenes contents were observed to reduce but with a corresponding increase in the mono-aromatics [76]. Vichaphund et al. [93] also studied the effect of Nickel catalyst incorporated in the HZSM-5 zeolite and compared the result with that obtained from HZSM-5 zeolite alone. They observed a higher aromatic content when HZSM-5 was used and a low naphthalene content for the Ni/HZSM-5 catalyst. This was attributed to the formation of tetralinic species when naphthalene acted on the Ni site by hydrogenation and a further crack of the tetralinic specie on the acid site to form benzene, toluene, xylene (BTX).

Moreover, diffusion of larger molecules into the inner pores of the HBeta catalyst is aided by its

large pore diameter, which allows a higher amount of pyrolytic products inclusive of polar aromatics to be broken down into smaller fractions in the kerosene range liquefaction. Dung et al. [94] recorded a reduction in poly and polar aromatic hydrocarbons and an increase in the light fraction from relatively 50 wt% to more than 70 wt%, when they carried out a study on the catalytic pyrolysis of waste tyres utilizing the cubic mesoporous silica synthesized with ruthenium (Ru/SBA-1) catalyst. It was explained that the element, ruthenium, reduced the content of particulate polycyclic aromatic hydrocarbons (PPAHs) through catalyzed hydrogenation reaction and lowered saturates content in the oil through hydrogenolysis [94]. Furthermore, composite materials such as HY/MCM-41 catalyst, which have large pore size and wide surface acidity, have been developed. The core-shell HY/MCM-41 catalyst exhibited an active catalytic pattern in the promotion of the liquid oil. Valuable aromatic hydrocarbons such as ethylbenzene and toluene were present in large amounts compared to those obtained with pure HY and MCM-41 catalysts. This was due to the acidity balance between the micropore and mesopore layers of the core-shell HY/MCM-41 catalyst coupled with the presence of a bimodal pore size distribution [73].

Apart from the zeolite catalysts, other bases, acid, or natural catalysts have been used in the catalytic pyrolysis of the waste tyre. For example, a high yield of aromatic hydrocarbon was recorded by Shah [12], who pyrolyzed waste tyre in the presence of calcium carbide catalysts. They recorded an output of 45 wt% aromatic, 35 wt% aliphatic, and 20 wt% of polar hydrocarbons, which were attributed to the styrene-butadiene rubber (SBR) in the tyres. In studying the effect of Al_2O_3 on the composition of the pyro-oil, Shah et al. [95] recorded a higher concentration of polar compounds (40%) and the lower concentration of aliphatic hydrocarbons. At the same time, no significant change was noticed for the aromatic hydrocarbon.

Light olefins generation from the pyro oil has gotten little attention compared to that of aromatics, gas composition and oil quality. Only a handful of researchers have recorded the challenges of light olefin production. Witpathomwong et al. [96] investigated the activity and selectivity of silica mesoporous MCM-48 and Ru/MCM-48 for waste tyres pyrolysis and noted that the utilization of Ru/MCM-48 catalyst produced light olefins two times more than the non-catalytic pyrolysis. It has also been recorded that light olefins in pyro-oil reached a high yield of 29.9% when He [77] studied catalytic pyrolysis of waste tyres with nano-HZSM-5/ γ - Al_2O_3 zeolites. The increased amount of aromatic compounds associated with most catalytic pyrolysis serves as an indication that the pyrolysis oil can be potentially harnessed as a chemical feedstock in different industries [74].

4.4. Effect of catalyst on physical properties of pyro-oil

The presence of a catalyst influences the physical properties of the pyro-oil, such as the viscosity, flash point, and density, which are some of the significant characteristics of any fossil fuel production. Shah et al. [13] obtained a more useful oil with closer physical properties value with that of diesel fuel when base catalysts were used. Using MgO and CaCO_3 as catalysts, they recorded comparable values of specific gravity, viscosity, and kinematic viscosity of oils for both catalytic pyrolysis and diesel fuel. When the CaCO_3 catalyst was used, they recorded a flashpoint value similar to that of diesel fuel, but a lower value was obtained with the MgO catalyst. However, for both catalysts, the sulphur content was close to that of diesel fuel. From the distillation data and fuel tests conducted, they concluded that the pyro-oil gotten from the catalytic pyrolysis with CaCO_3 and MgO satisfied the current specifications of diesel fuel. Hooshmand and Zandi-Atashbar [17] also

attained near values of density and kinematic viscosity with that of diesel fuel when $MgCl_2$, another base catalyst, was used. However, the flashpoint and cetane numbers were less than that of diesel fuel.

Moreover, the gross calorific value of the oil was determined as 42.1 MJ/kg. The high calorific value of the oil implies that it can be applied directly as a fuel. A lower flash point was also reported by Ayanoglu and Yumrutaş [83] in the presence of CaO and NZ catalyst, which indicates that there is an existence of more volatile fuel in the oil. The density, viscosity, and water content values of the pyro-oil were close to that of diesel fuel. The lower heating value (LHV) is another significant aspect of fuel. The LHV of pyro-oil, quantified as 41000 kJ/kg was observed to be approximately that of diesel fuel with a value of 42700 kJ/kg. In comparison with diesel fuel, the density of the non-catalytic oil was of higher value, whereas that of catalytic pyrolysis was similar to the value of diesel fuel. According to Fahed [79] the low viscosity of the oil indicates the positive characteristics in the handling and transporting of the oil.

Osayi and Osifo [97], in their investigation, used the zeolite NaY catalyst to compare the physical properties of pyro-oil obtained from catalytic pyrolysis with those obtained from non-catalysis in literature and commercial diesel. They reported an insignificant effect on the density, viscosity, pour point, and flashpoint of the catalytic pyro-oil. However, significant modifications were noticed in the catalytic pyro-oil fuel properties such as refractive index, high heating value, pH value, and sulphur content. In comparing the refractive index of both oil, they observed that the pyro-oil gave a refractive index of 1.514, which was lower than that of the un-catalyzed oil but closer to that of commercial diesel (1.45–1.475). This enhancement in the refractive index indicates that the pyro-oil auto-ignition performance would be better.

4.5. Effect of catalyst on produced gases

Many researchers have recorded a boost in the production of gases during catalytic pyrolysis, especially with the acid catalysts. They also noted that gases such as CO, H₂, CO₂, and CH₄ were present in the gas composition. Hijazi et al. [98] compared the gas yield from thermal pyrolysis and the Hbeta catalyst. They reported a rise in the gas yield from 20% to 28%. However, when the Hbeta was doped with Pd metal, the oil yield was significantly increased to 37%. They explained that the Pd metal sites affected dehydrogenation-hydrogenation reactions, which brought about the improved catalytic activity of the Pd/Hbeta catalyst. Arabiourrutia et al. [87] utilized HZSM-5 and HY zeolites for tyre pyrolysis in a conical spouted bed reactor at 425 and 500 °C. They observed an increase in the gas yield, notably higher contents of propene and butadiene in the presence of the HZSM-5 zeolite catalyst.

Moreover, it has been recorded that in the application of a zeolite catalyst, the concentration of carbon monoxide and carbon dioxide is reduced. At the same time, the other gases consisting of hydrogen, ethane, ethene, butane increased remarkably [72]. The decrease in carbon monoxide was also recorded by Kordoghli et al. [21] when they used MgO/oyster shell particles to pyrolyze waste tyre. Moreover, there was an increase in H₂, CH₄, and C₂H₆ gases, which indicates that the gas yield has significant energy content.

Hydrogen, considered as a clean energy source, is generated from the waste tyre and is intended to play a significant part in energy systems for the future; hence the attention is given to it. Elbaba and Williams [99] investigated the production of hydrogen from catalytic pyrolysis of waste tyres

using a two-stage fixed bed reactor and Ni/Al₂O₃ catalyst. The effect of catalyst/tyre ratio and operating temperature were investigated. They reported that hydrogen production was at 7.19 wt% with a catalyst/tyre ratio of 0.5, which increased significantly to 20.0 wt% at a ratio of 2.0. When the temperature was raised from 600 to 900 °C, a gas yield increase from 14.3 to 56.8 wt% was observed alongside an increase in the hydrogen yield from 3.2 to 13.1 wt%. Furthermore, increasing the catalyst/tyre ratio reduced the amount of carbon deposited on the catalyst. MgO-based catalyst was also found to increase the amount of H₂ while reducing the amount of H₂S, which is a good recommendation for the production of valuable energetic gases through thermochemical decomposition [14]. The high gross heating value of the pyrolytic gas (2900 J/g) makes it suitable to be used directly in providing the energy needed for the overall process. The gas has enough energy to meet the demand of the process, make up for heat losses, or use it in other ways [100].

4.6. Effect of catalyst on char

Based on the efficiency of the catalyst to carry out the chemical reaction at temperatures in the range 400–500 °C, the catalytic pyrolysis of the waste tyre may effect changes in the chemical composition of the char. Kordoghli et al. [14] recorded a higher heating value (HHV) of between 9.16–15.41 MJ/kg in the solid residue when CaCO₃ catalyst was used. In comparison with non-catalytic pyrolysis, the presence of the catalyst caused molecules containing oxygen to be retained in the char. These solids, when dried, are powdery in texture can be applied directly as a co-combustion fuel with other solid fuels rich in carbon. For example, co-combustion of waste tyre char with biomass will improve the burning performances and, thus, the overall energy efficiency of the process. Ayanoglu and Yumrutaş [83] observed that the surface area and structure of the char from the catalytic pyrolysis with CaO and natural zeolite (NZ) were similar to commercial carbon black. The char was reported to contain high carbon content, which increased with the combustion yield. Thus, the char could be applied as an activated carbon absorbent material. Besides, the high volatile matter and low ash content are underlying factors needed to manufacture the absorbents, as mentioned earlier. Hooshmand and Zandi-Atashbar [17] used MgCl₂ catalyst under the argon atmosphere to decompose the waste tyre. The generated solid residue was activated with physical steam, and the surface area (1296 m²/g) was compared with that of commercial activated carbons (over 1000 m²/g). They concluded that the activated char could be applied in the same way as commercial activated carbon due to their close surface area. San Miguel et al. [101] also activated the acquired char using both physical and chemical activating methods. They explained that the use of physical processes was preferred in industrial applications due to the corrosive nature of the chemical process, notwithstanding the advantages associated with the chemical process such as lower operating temperature and higher activating yield. Other applications of the solid residue could be in the removal of heavy metal, toxic gases, and purification of wastewater due to its morphological closeness with the natural carbon black. Furthermore, it can act as a catalyst in the rubber manufacturing industries [75].

4.7. Cons and limitations of catalytic pyrolysis

As stated above, catalytic pyrolysis of waste tyres is an optimistic approach in the conversion of waste tyres to high value-added aromatics and olefins, which acts as important raw materials for the

production of premium products, such as plastics, solvents, synthetic fibres, and pharmaceuticals. However, challenges with this method have been encountered. For instance, deactivation of the catalyst by the formation of coke, which blocks the micropores of the catalyst, is a significant challenge associated with catalytic pyrolysis. Also, polycyclic aromatic hydrocarbons (PAH), which are generally recognized as mutagenic, carcinogenic, and environmentally unfriendly, were found to be present in the oil products, thus limiting the utilization of the oil [102]. Additionally, the desulphurization methods for the catalysts reforming are still under, and the high ash content in the produced char constricts the possibility of recycling and in tyre production [16]. Based on the catalyst used, the oil may need to undergo further treatments such as filtration, desulphurization, and hydro-treating before it can be applied as a fuel [15].

5. Future work and recommendation

Research into broad industrial applications of pyro-oil is significantly needed. Applications such as the production of lemon scent from limonene obtained from pyro-oil, use of benzene to produce plastics and resins, and in the production of dye and pesticides from toluene. A notable breakthrough would be a waste tyre pyrolysis system that can provide value-added products alongside generating its energy to run the system [70]. Also, sustainable ways to combat the high temperatures needed for this process should be investigated. One such approach could be in the utilization of solar energy by focusing solar irradiations with the help of photoactive catalysts.

Furthermore, the co-catalytic pyrolysis of waste tyre with biomass is gaining attention and should be optimized for higher product yield, aromatic selectivity, and reducing coke formation. Besides, higher efficiency catalysts for sulphur removal should be synthesized.

6. Conclusions

A review of literature related to the pyrolysis of the waste tyre has shown that the process is influenced by various parameters such as temperature, heating rate, reactor type, particle size and presence of catalyst. A wide range of reactor types such as fixed bed, rotary kiln, auger reactor, microwave reactor, and fluidized bed reactor and their influence on pyrolysis products has been reviewed. It is found that fast pyrolysis conditions favoured the production of oil products while higher temperatures and slow pyrolysis conditions caused the secondary reaction to take place, thus cracking the oil to gas. The feedstock of smaller particle size was found to aid char reduction while increasing the gas yield due to more reaction surface of the feedstock. The pyro-oil from waste tyre pyrolysis are chemically complex containing aromatic (such as benzene, limonene, xylene, etc.), aliphatic (such as alkanes), hetero-atom, and polar fraction. However, the liquid oil is of low quality due to the presence of high solid residues and impurities such as sulphur, nitrogen, and phosphorus. This led to increased interest in the catalytic pyrolysis of waste tyres. Catalytic pyrolysis is related with the improved fraction or yield and in addition, reduces the sulphur content in the pyro-oil. Acid catalysts such as zeolite, mesoporous and SAPOs are the most used in the pyrolysis of the waste tyre and they promote the cracking of the oil and increase gas yield due to their acidity and shape selectivity.

It should be noted that the presence of the zeolite catalysts also improved the refractive index of the oil and reduced the sulphur content. Furthermore, the positive effect of base catalysts such as

MgO and CaCO₃ has been reported by various authors, which includes an increase in the oil yield, reduction of carbon monoxide and sulphur. Despite the possible benefits associated with the catalytic pyrolysis process, limitations such as high energy input due to the low thermal conductivity of tyres, cost of catalyst, and catalyst deactivation and regeneration still abound. Also, the lack of experience in pilot and full-scale units of catalytic pyrolysis poses a challenge. For optimum reactor design, a detailed knowledge on the catalyst deactivation and regeneration is needed to successfully compare this process with the non-catalytic process in terms of material and operational cost. Furthermore, sustainable and environmentally friendly pyrolysis processes should be developed to boost the economic aspect of the process.

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Conflict of interests

All authors declare no conflicts of interest in this paper.

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