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ADVANCES IN UNDERSTANDING KINETIC MECHANISMS UNDERLYING WASTE GROUND TYRE RUBBER PYROLYSIS

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ABSTRACT

The depletion of natural resources and the need to reduce solid waste in urban areas have necessitated the incorporation of used materials such as waste ground tyre rubbers (WGTR), into manufacturing processes. As a result, techniques and recycling methods have been established to use tyres as feedstock for marketable products since tyres have a calorific value higher than coal and contain a significant amount of carbon black. Among several techniques, pyrolysis has emerged as the most appealing for treating WGTRs. This technique allows the recovery of valuable products like combustible gases, fuels and chemicals, and activated carbon. Studies have focused on understanding the mechanism underlying the WGTR pyrolysis through the establishment of mathematical models and reaction patterns to valorise WGTRs and efficiently produce marketable chemicals. This paper presents an overview of recent developments in understanding WGTR pyrolysis mechanisms. A general mechanism observed involves a first depolymerisation/condensation of the rubbers, then a degradation of the condensed products, and finally a devolatilisation of additives. Based on the limited information available on the chemicals' formation mechanism, it is assumed that limonene and isoprene are derived from natural rubber (NR), through a series of β-scission and depropagation reactions of polyisoprene and intramolecular cyclisation and scission of monomeric isoprene, respectively, with an equilibrium step of Diels-Alder reaction. The maximum yield of limonene and isoprene have been found to be 51% and 20.5% at temperature around 500°C respectively. The isoprene yield can be increased up to 37.57 % with the use of catalyst such as Calcium Oxide.

1. INTRODUCTION

Renewable sources and waste valorisation processes are gaining interest due to several factors, including eliminating global warming and society's significant dependence on the limited fossil sources for fuels and essential raw materials. Moreover, the remarkable increase in the number of vehicles worldwide coupled with the inadequate technical and economic waste tyres recycling methods have led waste tyres to be considered one of the severe pollution problems in waste disposal (Martinez et al., 2013).

However, the world market for light vehicles is increasing steeply. In 2018, the global production of motor vehicles was 98.1 million units, with the future growth estimated at 110 million units by 2025. Accordingly, the demand for tyres will also increase, imposing a significant challenge to reuse or dispose of this complex material after use (Association, 2019; Menares et al., 2020). The annual global increment of waste tyre is estimated to around 17 million tons, and it is expected to reach 1.2 billion tons per year by the late 2030s (J. Xu et al., 2021).

Tyres are made of 38% rubber, 30% fillers (carbon black, silica and carbon chalk), 16% reinforcing material (steel, rayon, nylon), 10% plasticizers (oils and resins), 4% vulcanisation agents (sulphur, zinc oxide, various chemicals), 1% antioxidants to counter ozone effect and material fatigue and 1% of miscellaneous (Nkosi & Muzenda, 2014). On the other hand, waste tyres (WT) is a problematic waste that belongs to a type of solid waste named "bulky" in waste management. They refer to tyres that have exceeded their useful lifespan in roadworthiness and are difficult to degrade under typical environmental conditions (Q. Chen et al., 2022; Ishola Felix et al., 2018). The need to reduce solid waste in cities and the depletion of natural resources have necessitated the incorporation of scrap material into productive processes; hence giving value to what would oth-

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erwise be deemed waste and reducing the consumption of natural resources (Ramirez-Canon et al., 2018).

Therefore, researchers have been interested in developing processes and recycling strategies for waste tyres. These strategies aim at reducing waste tyre effects on the environment and take advantage of them as feedstock for marketable products since they have a calorific value higher than coal and a considerable amount of carbon black when the char is significantly refined. Waste tyre management methods may be classified into three categories: i.e., i) direct disposal (landfilling and stockpiling); ii) material recovery and recycling (milling/grinding, re-treading, devulcanisation and civil engineering applications); and iii) thermal treatment with energy recovery (incineration, gasification and pyrolysis) (Isayev, 2005; Rowhani & Rainey, 2016; Viglasky et al., 2017).

Waste tyres thermochemical conversion is one of the attractive processes used for valorisation or disposal. Incineration and combustion of waste tyres are beautiful solutions for heat and power production in conventional coal-based plants. However, these processes are deemed inefficient since they do not cater for valuable product recovery from the different fractions of the tyres (rubber, metal, carbon black) (Menares et al., 2020).

The thermochemical process of gasification is a sub-stoichiometric oxidation of organic material. The process involves the use of air, oxygen, hydrogen or steam/water as a reaction agent. Despite the considerable variation of the process, typical gasifiers operate at temperature between 700 and 800°C and its energy efficiency is reported to be around 76% (Viglasky et al., 2017).

A technically attractive way and most promising recycling strategy for the thermochemical treatment of WTs that allows the recovery of valuable products such as combustible gases, fuels and chemicals and activated carbons is pyrolysis (Q. Chen et al., 2022). Pyrolysis is a process of thermally decomposing the organic volatile matter of tyres (mainly the rubber polymers) into low molecular weight products, liquids or gases (Aylón et al., 2010).

WT pyrolysis techniques can be classified into several types depending on the operating parameters, such as the heating rate, the volatile residence time and the temperature. A simple classification comprises a slow pyrolysis, fast pyrolysis and a catalytic pyrolysis.

Slow pyrolysis considers a slow pyrolytic decomposition at low temperatures and is characterised by low heating rates, relatively long solid and vapour residence times (in order of minutes to hours). The longer residence times lead to secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products. The primary objective of this type of pyrolysis is the char production, although tar and gases are also obtained (Martínez et al., 2013).

Unlike the slow pyrolysis, fast pyrolysis implies a rapid thermal decomposition and is characterised by higher heating rates. The process usually requires a feedstock with small particle sizes and devices with special design to allow removing the vapours released quickly. The fast pyrolysis is recognised as an effective conversion route for the production of liquid fuels, chemicals and derived products with higher yield, generally favoured by high heating rates with short hot zone residence times and rapid quenching of the volatile products (Martínez et al., 2013).

Catalytic pyrolysis refers to any pyrolytic process that comprises a catalytic material in the same process in order to favour or upgrade some yield or properties of the products. WGTR catalytic pyrolysis has been conducted for the production of single ring aromatic compounds in the liquid fraction such as benzene, toluene and xylenes (Martínez et al., 2013).

The WGTRs pyrolysis products include a pyrolysis oil (tyre-derived oil, TDO) which is the most important fraction for energy recovery (engine fuels) and recovery of valuable chemical products such as limonene, benzene, toluene, xylene (BTX). Additionally, gas and solid are also obtained, being the first used to fulfil the energy requirements of the pyrolysis process. While the solid product, also known as char, can be used for producing carbon black or activated carbon as an additive for improved asphaltic and concrete mixtures and can be applied in tyre manufacturing (Ma et al., 2020; McCullough et al., 2015; Menares et al., 2020).

Albeit pyrolysis of wastes appears simple in concept, the products are often low-value mixtures of hydrocarbons with an extensive compositional range, sometimes extending from light gases to coke. The composition of different pyrolysis products depends on the conditions used and on the composition of the tyre. For this reason, depending on the final objective of the pyrolysis, it is necessary to find the optimal conditions for the type of feedstock and the process operating parameters (B Acevedo & Barriocanal, 2015; Martínez et al., 2013).

Several researchers investigated the influence of WGTR pyrolysis parameters on the devolatilisation of rubber components pathways. These parameters include temperature, pressure, particle size, inert gas flow rates, types of pyrolysis atmospheres, reactor configuration and the use of catalysts. However, no general agreement could be found among these studies on the relationship between products yields and these parameters (Parthasarathy et al., 2016; Quek & Balasubramanian, 2012).

Researchers have used the pyrolysis of solid-state materials mechanisms in the endeavour of the valorisation of the waste tyre. The approach entails developing appropriate mathematical models and reaction patterns from the thermogravimetric analyser (TGA) data, a typical thermal method of material analysis. Hence, different models have been used, including kinetic, mass transfer, and heat diffusion models (Khiari et al., 2018).

The state of the art of waste tyre pyrolysis process was reviewed for the first time in literature by Martínez et al. (2013). They presented a comprehensive review of the process by stating the effects of the primary process conditions, including the size and composition of the feedstock, on the distributions and physicochemical properties of the pyrolysis products (gas, liquid and solid fractions).

Moreover, they pointed out the main properties of the pyrolytic products with special attention given to liquid fraction by highlighting its properties as an alternative fuel in compression ignition engines. However, Williams (2013), in their review of the pyrolysis process of waste tyres, pre-

sented the range of reactors used so far by pointing out the influence of the reactors on the product yield and gas and oil composition. They also showed the principal gases produced from the pyrolysis of waste tyres to be H_2, C_1 - C_4 hydrocarbons, CO_2, CO and H_2S. In addition, they reported on the upgrading of char to higher quality carbon black and activated carbon. They also used catalysts to upgrade the oil to an aromatic-rich chemical feedstock or hydrogen from waste tyres. Nkosi and Muzenda (2014) also presented a review of the pyrolysis process by highlighting the influence of the operating conditions and discussing the pyrolytic products. Moreover, they analysed the pyrolysis products market and the success and failures of the process.

J. Singh (2015) reviewed and discussed the tyre pyrolysis process and the applications of the derived products. They reported the characteristics of used tyres materials and recycling methods, the types and principles of pyrolysis, the pyrolysis products and their composition, concluding by the advantages of a waste tyre pyrolysis plant. Lewandowski et al. (2019) discussed the current use of different pyrolytic reactors, their constructions and operating principles regarding the yields of main products of waste tyre pyrolysis. They summarised and compared main products yields (oil, gas, coal) obtained in different reactors and by different authors. Januszewicz et al. (2020) also conducted a review on the technologies of limonene production from waste tyre pyrolysis. They showed that the conditions that facilitate increasing limonene yields (low temperature and pressure, fast heating rate and short residence time of volatile products in the reaction) are best obtained in the following reactors: Vacuum mechanical, fixed bed, inert gas and catalyst, fluidised bed and mechanical pyrolizers being the least efficient.

Recently, Jahirul et al. (2021) investigated the use of waste tyres as an alternative fuel to address the global problem of waste tyre management and environmental concerns. They reviewed recent publications on the topic and found that pyrolysis is the most common thermochemical method for addressing the waste tyre management issue due its simplicity, high recovery of liquid and solid materials, and low environmental impact. They concluded that the product yield and composition of waste tyre depends n reactor type and operating condition. The average production yield, char, syngas, and steel from waste tyre pyrolysis is 40-60%, 10-20%, and 10-15% by weight, with the favourable temperature range for the high yield of liquid oil being 450-500°C. Mavukwana and Sempuga (2022) also conducted a review on the analysis of the recent advances in waste tyre pyrolysis and gasification technologies. They concluded that a techno-economic analysis to compare the use of gasification/co-gasification of waste tyres with other solid-to-liquid processes is required, and that a solar assisted pyrolysis could offer energy/cost savings opportunities.

From the above, since pyrolysis of waste tyres has received particular attention in the 1990s, the kinetic theory was still in a state of considerable disarray and the devolatilisation mechanisms for tyre pyrolysis, in their formative stages. Since then, understanding the reaction dynamics involved in pyrolytic processes has evolved substantially, and the corresponding kinetic schemes have been refined to fully describe the entire tyre pyrolysis process. In light of this, this paper intends to provide a concise overview of the advances in understating the mechanisms underlying the waste tyres pyrolysis process.

In addition, this paper will review waste tyre pyrolysis in terms of the composition of the products from the pyrolysis process. The waste tyre pyrolysis mechanisms are presented in detail. The research related to the pyrolysis kinetics and modelling approach is also reviewed and discussed.

2. WASTE TYRE PYROLYSIS

2.1 Process description

Pyrolysis consists of a thermal decomposition of organic materials without oxygen, cracking them down to simpler organic compounds. It relies on the addition of heat to break chemical bonds, providing a mechanism by which organics decompose and vaporize. Most tyre pyrolysis processes operate within a temperature range of 250-500°C, although some are reported to run at up to 900°C. At temperatures above approximately 250°C, shredded tyres release higher amounts of oil and gases. In contrast, above 400°C, oil and solid tyre-derived char yield may decrease relative to gas production (Antoniou & Zabaniotou, 2013).

The rubber is heated in the reactor and consecutively, the rubber polymers break down into smaller molecules which eventually evaporate and exit from the reactor. These hot volatiles can be burned directly to produce power or condensed into an oily type liquid, called pyrolysis oil or bio-oil. Smaller molecules, unable to condense, remain as a gas and are burned as fuel. The minerals contained in the tyre, such as sulphur, zinc oxides etc., are removed as a solid (Viglasky et al., 2017).

A tyre pyrolysis process is an endothermic process. Thus, temperature exerts a remarkable effect in the products and conversion grade. If the temperature is around 450°C, the main product is liquid, a mixture of hydrocarbons depending on the waste material's initial composition. At a temperature above 700°C and due to further cracking of liquids, a mix of hydrogen and carbon monoxide (synthetic gas) becomes the primary product (Viglasky et al., 2017).

Thus, the nature of the feedstock and process conditions defines the properties of the pyrolysis products. For example, whole tyres contain fibres and steel, while shredded tyres have most steel, and sometimes most of the fibre removed. In addition, the reactor is an essential part of the pyrolysis process. Researchers have used a wide range of reactors, including fixed-bed (batch), fluidized-bed, rotary kiln, screw kiln, and spouted bed for scrap tyre pyrolysis (Lewandowski et al., 2019; Rowhani & Rainey, 2016; Viglasky et al., 2017). The process can be batch or continuous, according to pressure applied, i.e., at atmospheric or vacuum. The energy required for thermal devolatilisation of the scrap tyres can be in the form of directly-fired fuel, electrical induction and or microwaves. The process uses nitrogen or another inert gas as carrier gas. To some extent, the pyrolysis might require a catalyst to accelerate the process (Viglasky et al., 2017).

Pyrolysis products are gas, liquid and char. The liquid is the highly regarded and economically valuable fraction for its high heating value (>40 MJ/kg) and high-value chemicals (Q. Chen et al., 2022; Hita et al., 2016). Therefore, the most profitable reactor designs and process operating parameters allow higher liquid yields. A schematic of the WT pyrolysis process is shown in Figure 1.

The liquid fraction also called pyrolysis oil includes a wide range of compounds, such as alkanes, alkenes, aromatic compounds, and hydroxyl compounds (G. Zhang et al., 2021). Therefore, the tyre pyrolysis oil is a potential source of fuel and chemicals. The specific chemicals are separated from the bulk tyre oil through several techniques and depending on the composition and properties of the oil. The Most useful techniques are distillation, the widely used technique and most effective for separating volatile hydrocarbons form the oil, solvent extraction that involves the use of a solvent to selectively dissolve and extract certain components from the bulk tyre, fractional crystallisation that exploits the difference in solubility of components in a solution, adsorption that involves the attachment of certain components of the bulk tyre oil onto a solid surface known as an adsorbent, membrane separation that uses semipermeable membranes to separate components based on their size, polarity, or other properties, and, centrifugation that involves the use of centrifugal force to separate components based on their density (Drugkar et al., 2022; Farzad et al., 2021; Gollakota et al., 2016; Januszewicz et al., 2020; G. Zhang et al., 2021).

2.2 Operating parameters

WT pyrolysis is an endothermic process maintained by temperature in the reactor. Temperature emerges as the operating parameter that exerts a considerable effect on the product distribution and conversion grade.

Therefore, temperature is the parameter that significantly influences the pyrolysis process and the WGTR pyrolysis mechanisms. The heating rate and particle size interact in the heat transfer phenomena directly with the gas, liquid, and solid fraction distribution and their physicochemical properties (Martínez et al., 2013). The carrier gas flow and the atmosphere type also have a considerable effect in the process, controlling the occurrence of secondary pyrolysis reactions such as thermal cracking, repolymerisation, recondensation and/or char formation (Martínez et al., 2013). Other parameters such as pyrolysis time and hot volatiles residence time involved in the process also exert a remarkable effect.

Three phases are obtained from the WGTR pyrolysis process: solid, liquid, and gas. Their composition is related to the temperature of the thermal treatment. In addition, from the conversion point of view, 500°C appears to be the optimum temperature at atmospheric pressure since total tyre conversion is achieved (Aylón et al., 2005; M.F. Laresgoiti et al., 2000). The principal tyre compounds (NR, BR and SBR) remain in the pyrolytic carbon black at lower temperatures, showing a heterogeneous sticky-gummy feature (Martínez et al., 2013). At higher temperatures, there are no reported significant influence on the amount and characteristics of the pyrolysis products (González et al., 2001; M. F. Laresgoiti et al., 2000).

Gas yield increases with temperature due to substantial thermal cracking at high temperatures (Zabaniotou & Stavropoulos, 2003). Gas compounds and yields are susceptible to secondary reactions and heterogeneous reactions involving the inorganic compounds of a tyre. Therefore, the gas fraction behaviour in terms of composition, calorific value and yield are quite disparate among results reported in the literature (Martínez et al., 2013). It is expected that longer chain hydrocarbons decrease as temperature increases in favour of lighter hydrocarbons and H_2.

On the solid fraction, no significant changes in the yield are expected when pyrolysis temperature increases. Therefore, the amount of the solid fraction must be similar to the sum of the original char and the ash content. However, due to secondary reactions such as tar and char formation reactions, the solid fraction can be higher than the expected value. On the contrary, when the carrier gas has some oxygen content (CO_2 and/or steam), an increase in temperature can also promote a lower char yield, given the occurrence of gasification reactions (Betancur et al., 2009; Martínez et al., 2013).

However, the liquid yield of pyrolysis is almost stable or shows a maximum at around 450-500°C and decreases

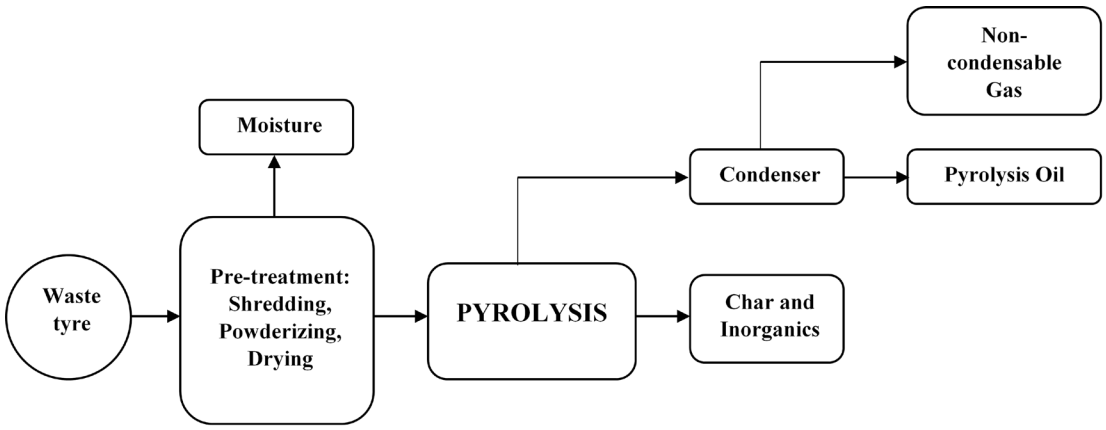

FIGURE 1: Waste tyre pyrolysis process schematic.

at higher temperatures. Simultaneously, the aromatic compounds in the liquid fraction increase. The increase in aromatic compounds is due to secondary reactions that modify the chemical properties and yields of the products, as mentioned previously on the influence on the gas products. Moreover, F. Xu et al. (2018) reported that the primary pyrolysis products of gases, alkenes and aromatics greatly vary when the temperature changes. The fraction of alkenes decreases with temperature increase due to secondary cracking of pyrolysis products in the temperature range of 600-800°C and then increases when the temperature reaches 800°C and above.

The yield of limonene, one of the alkenes' main products, increases at higher temperatures (around 450°C) and decreases when the temperature reaches 800°C. The decreasing of limonene content is attributed to the decomposition of D-limonene into aromatics due to secondary reactions such as cyclisation and aromatisation at high temperatures (N. Mkhize et al., 2016; F. Xu et al., 2018). However, the content of D-limonene shows an increase when the temperature is raised from 800°C to 1000°C due to some reactions such as the Diels-Alder reaction of isoprene (F. Xu et al., 2018). Sanchís et al. (2022) confirmed the influence of temperature profile on both the distribution and properties of products, when investigating the effect of different temperature profiles by using a single-auger pyrolysis reactor in an industrially relevant scale and two temperature profiles (425-550-775°C and 600-700-800°C). They found that the 425-550-775°C profile enhanced limonene production, while the raise of temperature favoured the production of single-ring aromatics, particularly benzene, toluene, ethylbenzene and xylenes in TDO.

The previous observation was made for another chemical of tyre oil, i.e., indene. The yield of indene shows an increase with temperature increase up to 500°C then decreases at higher temperatures.

Next to temperature, heating rate plays a vital role in controlling the product yield of pyrolysis. An increase in the heating rate shifts to higher temperatures the weight loss profile in the thermogravimetric analysis. Leung and Wang (1998) reported that with increasing heating rate, the weight loss regions shift to a higher temperature range, the weight loss rate increased and the reaction time shortened quickly with no noticeable change in the total weight loss. The apparent activation energy and frequency factor also increase with increasing heating rate, increasing the pyrolysis reaction's difficulties.

Pressure is another parameter that influences the production of chemicals from pyrolysis. Decreasing the pyrolysis pressure leads to a decrease in the residence time (Roy et al., 1997). Hence, the formation of undesired products and the destruction of desirable chemicals, such as limonene, are minimised. Roy et al. (1997) found that dl-limonene decreased with increasing pyrolysis pressure. Therefore, it is preferable to perform rubber pyrolysis at low pressures to produce chemicals of higher commercial value. Ma et al. (2020), while studying the effect of residence time and pressure on limonene at pressurized pyrolysis of waste tyre, found that, at the constant residence time, pressure exhibits a positive effect on limonene production. The yield of limonene was found to increase by 73% and limonene concentrations in TDO increased by 60%, as the pressure increased from 0.1 MPa to 1.0 MPa and at a constant residence time of 30 s.

In an effort to improve the quality of the products and the selectivity of the WT pyrolysis process, the use of catalysts has merged as an interesting alternative. The catalysts contribute to increased yields of valuable aromatic compounds, improve the quality of the resulting products, such as TPO, and help reduce the presence of sulphur-containing compounds. They enable the conversion of waste tyres into more valuable chemical products, thereby enhancing the economic and environmental aspects of waste tyre disposal (Miriam Arabiourrutia et al., 2020; Williams, 2013). A wide range of catalysts have been proposed in the literature for WT valorisation, with zeolites being the most commonly used due to their capacity for the production of valuable chemicals, such as BTX and light olefins (Miriam Arabiourrutia et al., 2020). Notable microporous acid zeolites used include HZSM-5 and HY, with differences in pores sizes influencing their selectivity. HZMS-5 favours monomolecular cracking, while HY has a higher aromatization capacity due to its higher acid density (Rowhani & Rainey, 2016; Williams, 2013). Other zeolites like Hβ, HZSM-22, HMOR, SAPO-11, and ZSM-22 have been explored for tyre pyrolysis. Their varying pore structures and acidities contribute to different product distributions, with some favouring gas and aromatic production (W. Li et al., 2016; Muenpol et al., 2015). Base catalysts, while less active than acid catalysts for C-C bond cleavage, facilitate hydrogenation, isomerization, alkylation, and reactions involving heteroatoms. MgO and CaO are commonly used base catalysts for tyre pyrolysis, improving the quality of the liquid and enhancing cracking activity (Kordoghli, Khiari, et al., 2017; Kordoghli, Paraschiv, et al., 2017; Shah et al., 2008). Carbonates, hydroxides, and natural materials like dolomite, olivine, and red mud have also been tested. Some of these materials, like dolomite and olivine, exhibit sulphur removal capabilities, resulting in TPO with low sulphur content (Choi et al., 2016; Demirbas et al., 2016; X. Zhang et al., 2008).

Different reactor configurations have been employed for catalytic pyrolysis, including fixed bed batch reactors, bench-scale units (fluidized beds, spouted beds, and rotary reactors), and pilot plant-scale systems operating under continuous fast pyrolysis. The catalysts were placed either in situ or ex situ in a second reactor (Miriam Arabiourrutia et al., 2020). However, the majority of studies are at the preliminary or laboratory scale. In the in situ catalytic pyrolysis, the catalyst is placed within the same reactor as the pyrolysis process. San Miguel et al. (2006) conducted an experiment where they integrated in situ zeolites into a thermobalance sample container coupled to a GC/MS. They observed that these catalysts exhibited a significant preference for producing BTX, while simultaneously reducing olefinic hydrocarbons. In the ex situ method, a second reactor is employed for the catalytic cracking of pyrolysis volatiles, separated from the pyrolysis reactor. Ex situ catalytic cracking of tyre pyrolysis volatile has primarily been studied in fixed bed reactors, with various

configurations been explored (Miriam Arabiourrutia et al., 2020). (Kordoghli, Paraschiv, et al., 2017) investigated the pyrolysis batches scrap at 500°C and the in-line cracking of the stream leaving the first reactor on different catalysts, such as ZSM-5, Al_2O_3, $CaCO_3$ and MgO. They found that $CaCO_3$ was the most influence catalyst. The direct contact of $CaCO_3$ with the tyres led to an augmentation of total conversion from 54.59% to 63.92% in TGA tests, and from 54.9% to 62.7% in bench-scale installation. In contact just with the pyrolysis vapours, the tyre conversion only reached 59.7%. Boxiong et al. (2007) conducted a study involving the batch catalytic pyrolysis of waste tyre using ZMS-5 and USY catalyst. The setup used comprised two fixed bed reactors, with the pyrolysis step conducted at a temperature of 500°C and the subsequent catalytic cracking taking place within the temperature range of 350-500°C. They found that the influence of catalysts was to reduce the yield of oil with a consequent increase in the gas yield and high concentrations of single aromatics. The concentrations of toluene in the light fraction from un-catalysed oil was of 3.04wt%, which increased to 5.68wt% with the ZSM-5 and 13.70wt% with the USY catalyst. Williams and Brindle (2003) also investigated batch pyrolysis of waste tyres at a temperature of 500°C and a subsequent in-line catalytic cracking of the pyrolysis volatiles using HY and HZSM-5 zeolites within the temperature range of 430 to 600°C, to maximise the concentration of single ring aromatic compounds. They observed an increase in the concentration of single ring compounds in the oil, with toluene reaching 20wt%, o-xylene 7wt%, benzene 5wt% and m/p xylenes 20wt%.

Furthermore, Choi et al. (2016) developed an innovative process involving two in-line reactors operating continuously, to produce a pyrolysis oil with a low sulphur content. The initial reactor was an auger reactor where partial degradation of waste tyres occurred at a temperature of 340°C, and the subsequent reactor was a fluidized bed reactor operated at 520°C and using various catalysts, such as dolomite and olivine. They obtained the lowest sulphur content of 0.45wt% using calcined olivine. More recently, Osorio-Vargas et al. (2022) examined the catalytic pyrolysis of WT using noble-meal based catalysts supported on nanostructured titanates nanotubes (NT-Ti). The investigation focused on understanding the product distribution and the yield of valuable hydrocarbons, specifically benzene, toluene, xylene (BTX), and p-cymene. The catalysts employed, denoted M/NT-Ti (with M representing Pd, Pt, or Au), exhibited small nanoparticle sizes ranging from 1.8 to 2.2 nanometers and a uniform pore size distribution due to the textual characteristics of the support material. They found that the catalytic pyrolysis significantly increased the production of monoaromatic compounds, with Pd-based catalyst being the most effective, leading to higher yields of BTX and p-cymene compared to non-catalysed pyrolysis. The catalyst exhibited a bifunctional nature, favouring cyclisation, isomerisation, and aromatisation reactions on both metallic and acidic sites, enhancing catalytic activity. Additionally, the study examined the pyrolysis of individual WT polymers and D,L-Limonene to understand the complex reaction pathways.

Table 1 summarises the influence of pyrolysis parameters on WT pyrolysis reaction mechanism by highlighting differences in products yields and some chemical concentrations from the literature.

3. WASTE TYRE PYROLYSIS MECHANISMS

3.1 Introduction

Pyrolysis is defined as the thermal treatment of WTs under inert conditions to yield pyro-gas, tyre-derived oil (TDO) and pyro-char. TDO is the main pyrolysis product fraction on a weight basis, and as a liquid, it is relatively easy to handle. Therefore, TDO is the most interesting pyrolysis product and a potential source for recovering valuable chemicals. At the same time, the resulting residues can be upgraded to liquid fuels comparable to conventional petroleum-derived products and fuels (N. Mkhize et al., 2019).

As previously mentioned, several studies have been performed to investigate the pyrolysis parameters of WTs to oil. However, no general agreement could be found among these studies on the relationship between oil yields and these parameters.

Hence, the pyrolysis process of waste tyres has been investigated in detail over the decades using numerous approaches by various researchers to understand its kinetics and mechanisms.

For instance, J. Chen et al. (2001) investigated thermogravimetrically the pyrolysis kinetics of passenger car tyre (PCT) and truck tyre (TT) in N_2 for heating rates of 5, 10, 20 and 30°C /min and temperature ranging from 100 to 900°C. They found that the pyrolysis reaction begins with the dehydration and devolatilisation of processing oils, followed by the devolatilisation of natural rubber or butadiene rubber. Using Friedman's method, they also reported the average kinetic parameters of E=147.95±0.21 $kJ.mol^{-1}$, A=(6.295±1.275) x 1010 min^{-1}, and n=1.81±0.18 for the two tyres that they observed to behave similarly in pyrolysis devolatilisation.

In the same way, Iwarere and Mkhize (2019) conducted a kinetic mechanism study of two types of WT (TT and PCT) pyrolysis based on the rubbery fractions devolatilisation at heating rates 10 to 50°C/min. They used two model-free methods (Freidman and Kissinger) and observed that the reaction progress profile of the TT matches that of the PCT, with the gradient of the TT profile being steeper compared to the PCT. Moreover, they reported that the TT profile is characterised by one prominent peak attributed to the natural rubber, the main rubbery fraction of the TT. However, two distinctive peaks were observed in the devolatilisation of the PCT. Peak one was sought to be the NR, whereas peak two was associated with synthetic rubber (BR and SBR). Therefore, the authors concluded that there is a high potential for stepwise pyrolysis of the fractions from tyre rubber, particularly PCT, which may benefit the fractional recovery of the valuable chemicals from the WTs.

Seidelt et al. (2006) showed that tyres are made up of the three main components, i.e., NR (polyisoprene), styrene-butadiene rubber copolymer (SBR) and additives (sulphur, zinc oxide (ZnO), carbon black). The derivative thermogravimetric (DTG) curves of these components in

TABLE 1: Influence of WT pyrolysis parameters on products and chemicals production.

Ref.	Material/ Energetic potential	Reactor configuration	Pyrolysis parameters			Tyre pyrolysis products			Chemicals yields in Pyrolytic oil	
			Temp. / Time	Heating rate	Pressure/ Catalyst	Gas %	Solid %	Liquid %	Limonene %	Indene %
J. A. Conesa et al. (2004)	Tyre (4 mm) NCV: 7671.5 kcal/kg	Fixed Bed	450 750 1000	-	-	- 25.1/ 22.15	35.2/13 37.2/14 37.6/16	37.8/25 10.9/13 <0.01	6.9/4.1 g/kg 0.2/1.1 g/kg -	0.3/0.4g/kg 1.6/1.8g/kg
S.-Q. Li et al. (2004)	Shredded scrap tyres (13-15 mm) LHV: 34923 kJ/kg	Rotary Kiln	450 500 550 600 650	-	-20 to -10 Pa	13.1 13.6 15.5 18.0 18.3	43.0 41.3 39.3 39.3 38.8	43.0 45.1 44.6 42.9 53.7	5.440 1.883 0.419 0.122 0.070	0.831 0.381 0.900 0.447 0.382
M. Laresgoiti et al. (2004)	Car tyre (2-3 cm wide) GCV: 31.8 MJ/kg	Autoclave	300 400 500 600 700	15°C/ min	-	7.6 19.3 17.2 17.6 17.8	87.6 55.9 44.8 44.2 43.7	4.8 24.8 38.0 38.2 38.5	21.07 8.22 5.12 3.19 3.29	0.77 0.43 0.90 0.64 0.60
Rofiqul et al. (2007)	Heavy automotive waste tyre (2, 4 and 12 cm^3) HHV: 33.30 MJ/kg	Fixed-bed fire-tube heating reactor	425 475 525 575	15°C/ min optimal	Slightly above the atmospheric	8 9 12.5 18.6	39.5 37 35.5 33	52 55 51 48	50.8 50.86 24.84 21.24	-
M Arabiourrutia et al. (2007)	Scrap car tyres (0.63- 1 mm)	Conical spouted bed reactor	425 500 550 610	-	-	0.70 3.50 3.05 3.18	34 34	30.48 29.30 27.29 23.70	23.93 16.94 13.59 6.34	0.46 1.94 1.15 1.40
G. Lopez et al. (2010)	Tyre (3 g/min) HHV: 38.847 kJ/kg	Conical Spouted Bed	425 600			~2 ~7.5	33.9 35.8		19 <1	-
Islam et al. (2011)	Waste Truck tyre (4 cm^3)	Fixed Bed	375 425 475 525 575	-	-	7.5 8 9 12.5 18	45 39 36 35 35	47 53 55 52 47	50.86	-
Bajus and Olahová (2011)	Automotive scrap tyres (1-3 cm^2) HHV: 38.847 kJ/kg	Batch reactor	450 570	16.5, 9 and 7.5°C/ min	-	11.1 9.3	46.3 40.7	42.6 50.0	9.0 4.6	-
Beatriz Acevedo and Barriocanal (2014)	Tyre crumbs	Rotary Oven Fixed bed	850 850	5°C/min	-	35 3.5	28 38	25 55	5.12 21.58	9.74 3.85
Alvarez et al. (2017)	Waste truck tyre (2.8- 3.3 mm) HHV: 38.2 MJ/kg	Conical spouted bed reactor	425 475 575	10^3-10^4°C/s	-	3.7 5.9 10.1	37.9 35.9 35.9	58.4 58.2 54.0	21.05 22.84 7.04	0.26 0.30 1.09
Song et al. (2017)	Tyre rubber powder (0.6 mm) LHV: 40235 kJ/kg	Microwave	10 20 30 mins	-	-	9.4 11 12	54 44.8 43	36 44 45	8.61 9.92 9.83	1.01 1.47 1.58
R. K. Singh et al. (2018)	LVT MVT HVT	Batch reactor	650 750 750	20°C/ min	Max 3 atm	8.5 12 9	39 42 27	51 45.5 63.5	11.11 21.22 12.75	0.45 0.80 0.44
Ma et al. (2020)	TT Powder	Fixed-bed	500	20°C/ min	0.1MPa 1.5MPa		33 53	45 32	6.69 6.75	-
Williams and Brindle (2002)	Used tyres 1.0-1.4mm	2 Fixed beds	500/ 430	10°C/ min	ZSM-5 HY	15.1 16.8	38 37.3	42.9 38.7	-	-
Shah et al. (2008)	Tyres 5 10 mm	Fixed Bed	400 400	5°C/min	MgO $CaCO_3$	19.3 31.9	53.5 38.9	27 29.2	-	-
Miandad et al. (2018)	WT granules (2-3.5mm)	Pilot scale reactor	450	10°C/ min	No-catalytic Nat. Zeolite H-SDUSY Al_2O_3 $Ca(OH)_2$	20.0 24.6 37.4 34.1 18.4	40.0 53.4 42.6 33.9 55.6	40.0 22.0 20.0 32.0 26.0	-	-

the proper ratios were superimposed on DTG curves of tyres under study through a trial-and-error process. The author performed a similarity merging to show a good agreement with experimental results using kinetic parameters obtained for each component. B Danon et al. (2015) investigated the pyrolytic devolatilisation behaviour of four rubbers (NR, Synthetic polyisoprene, BR and SBR) at five heating rates (2, 5, 10, 15 and 20°C/min), using combined model-free and model-based kinetics. They concluded that the devolatilisation of the four rubbers consisted of two separate zones of weight loss (devolatilisation reactions), which were, primary depolymerisation/condensation of the rubbers and (consecutive) degradation of the condensed product. They also reported a third devolatilisation reaction for SBR, which represented the devolatilisation of additives.

Han et al. (2018) applied the thermogravimetric analyser combined with a mass spectrometer to understand the waste tyre pyrolysis mechanism. They demonstrated that DTG curves of waste pyrolysis had a bimodal peak at 250-500°C and a small peak at 600-800°C. Moreover, the evolution of gas products detected by MS and the functional groups on the surface of the residue char identified by FTIR also proved that tyre pyrolysis could be divided into four stages. The first stage occurred below 320°C and was associated with minor mass loss due to water vaporisation and plasticiser decomposition. The second stage was attributed to the devolatilisation of NR at 320-400°C. The third stage took place at 400-520°C and relates to the devolatilisation of synthetic rubber, while an insignificant weight loss was observed at the fourth stage above 520°C. Recently, Gauthier-Maradei et al. (2019) presented a study focused on modelling a fixed bed reactor involving the determination of kinetic parameters to predict the tyre rubber (TR) pyrolysis through two steps. Firstly, the establishment of a reaction mechanism for degradation of TR based on the decomposition of its three main polymer compounds (NR, BR and SBR) using a differential scanning calorimetry (DSC). Subsequently, the kinetic parameters for each reaction were determined by the Borchardt-Daniels method using the heat flow obtained by DSC. In the second step, the authors included the chemical mechanism and the associated kinetic parameters in a developed mathematical model of a fixed bed reactor at a laboratory scale considering mass and energy balances. They proposed a general mechanism constituted by six reaction steps; three associated with primary pyrolysis (exothermic), two to secondary pyrolysis (endothermic) and one to a post-cracking reaction (exothermic, was observed for NR and SBR). Moreover, for the model proposed at 600°C, the scrap tyre rubber begins its thermal degradation after 11 min of reaction, obtaining a maximal liquid production at a reaction time of 18 min. The total consumption of the intermediate compounds occurs.

From the points discussed above, it can be deduced that there has been substantial literature data mainly focusing on the kinetic mechanism of tyre components devolatilisation. There seem to be agreements on the observations. However, little is known about product formation kinetics. Therefore, some recent research has been conducted to optimize pyrolysis process parameters and establish mathematical modelling to bring more insights into understanding the kinetic mechanism for the production of specific products.

For example, Ngxangxa (2016) developed both qualitative and quantitative gas chromatography-mass spectrometric (GC-MS) and comprehensive two-dimensional gas chromatography (GC×GC) methods for tyre derived oil (TDO) analysis of selected market-value compounds in TDOs. The abundant constituents present in the TDO were DL-limonene, p-cymene, benzothiazole, ethylbenzene, toluene, p-xylene, 3-ethyl toluene and α-terpinolene. N. M. Mkhize (2018), through a modification of the existing waste tyre pyrolysis processes, developed novel methods critical to maximising the DL-limonene yield in the pyrolysis oil with an improvement in the total TDO yield and quality [high quality characterised by high DL-limonene content and fewer heteroatom compounds (nitrogen-, oxygen- and sulphur-compounds, mainly benzothiazole)] observed. In another study, N. Mkhize et al. (2019) investigated the formation of isoprene and DL-limonene during WT pyrolysis in terms of the effect of heating rate (up to 100°C/min). They used a thermogravimetric analyser coupled with mass spectrometry (TGA/MS and reported that the peak temperature of both the isoprene and DL-limonene formation reactions increased with the increase in the heating rate. The latter is more significant than the one in isoprene. In addition, it was found that the maximum DL-limonene formation rate was relatively higher compared to maximum isoprene formation rate as the heating rate increased. Moreover, the model parameter estimation through the Kissinger method provided activation energies of approx. 133 and 115 $kJ.mol^{-1}$ for isoprene and DL-limonene formation reactions, respectively. Investigating the primary pyrolysis characteristics of WTs under different temperatures, Ding et al. (2015) adopted a setup based on an analytical pyrolyser coupled with gas chromatography/mass spectrometry (Py-GC/MS). They reported that the primary pyrolysis products of WT at 600°C were alkenes rather than alkanes or aromatics. Isoprene (18.7%) and D-limonene (22.9%) were found to represent the main compounds of chain alkenes and cyclic alkenes, respectively. The yield and selectivity of alkenes achieved the optimal at 600°C. To further understand the pyrolytic mechanism of WT, D-limonene was pyrolysed in Py-GC/MS to investigate the degradation procedure. It was indicated that, at low temperatures (≤ 500°C), the isomerisation reaction dominated the conversion process. When the temperature rose to 600°C and above, reactions such as internal cleavage of the C-C bond, intermolecular hydrogen transfer, and cyclisation to aromatics, were dominant. The bicyclic aromatics, such as indene and naphthalene, were also detected when the temperature was higher than 650°C. In addition, the TG-FTIR experiment exhibited that WT went through ring-opening and re-cyclisation reactions as the temperature exceeded a relatively high degree.

Menares et al. (2020) conducted a study of fast pyrolysis of WTs by quasi-isothermal thermogravimetric (TGA) analysis, kinetic modelling and analytical pyrolyser coupled with gas chromatography/mass spectrometry (Py-GC/MS). They reported that at up to 482°C, the WTs pyrolysis

is characterised by devolatilisation/condensation and depropagation reactions, while at higher temperatures, the cyclisation and aromatisation of primary products take place to form mostly monoaromatics. At temperatures below 500°C, isoprene (20.5%) and limonene (51%) were the major compounds detected (max. selectivity 71%) while at temperatures above 600°C, the formation of monoaromatics and gases was favoured with limonene and isoprene compositions being ruled by the equilibrated Diels-Alder reaction. Moreover, the kinetic parameters determined by model-based and isoconversional methods were in good agreement (101-176 kJ.mol^{-1}). In addition, proposing a simplified reaction map for WTs pyrolysis to explain the changes caused by the temperature in products composition, the authors concluded that the integration of TGA, Py-GC/MS and modelling allows understanding the reaction pathways controlling the WTs pyrolysis and, are the basis for estimating accurate kinetic parameters.

More recently, Q. Chen et al. (2022) investigated the thermal decomposition characteristics, reaction kinetics, high value-added products production and potential mechanisms during WT pyrolysis in the presence of Calcium Oxide using Thermogravimetry-Fourier Transform Infrared spectrometer (TG-FTIR) and Pyrolyser-Gas Chromatography/Mass Spectrometry (Py-GC/MS). They found that CaO accelerated depolymerisation terms of reducing the reaction temperature, with an effect on kinetic parameters. Additionally, the content of D-limonene increased by 13.76% and that of isoprene by 37.57%.

From the above, the kinetic mechanism studies on the thermochemical treatment of waste tyres mainly focused on tracking the devolatilisation of the main components of the tyre. A general mechanism can be observed from the literature and involves a first depolymerisation/condensation of the rubbers, a consecutive degradation of the condensed products and a third devolatilisation of additives. An insufficiency has been observed in works tracking the formation of valuable chemicals. From the limited data on the tracking of limonene and isoprene, it is broadly accepted that these two products are produced from NR, through a series of β-scission and depropagation reactions of polyisoprene and, by intramolecular cyclisation and scission of monomeric isoprene, respectively, with an equilibrium step of Diels-Alder reaction, Figure 2 (Menares et al., 2020; N. Mkhize et al., 2016).

The following sections discuss the most used methods and models for the solid-state kinetic mechanism study. A particular accent will be on the WTs pyrolysis mechanism study methods.

In a study to understand the influence of the variations in tyre composition on thermal degradation, Williams and Besler (1995) heated in a TGA, three different tyres (particle size < 1m and mass ~ 20 mg) at different heating rates (5, 20, 40 or 80 K/min) and compared the results with thermograms of three rubber compounds (NR, BR, and SBR). They found that areas of significant weight loss on the thermograms correspond to the weight loss patterns of one or more of the three rubbers and could derive kinetic parameters using the Arrhenius equation and its derived equations. Moreover, Williams and Besler's major initial pyrolysis products were isoprene, dipentene or other dimers. A further reaction resulted in the formation of a wide variety of compounds, directly by polymer chain scission or via degradation products of isoprene and dipentene, or via secondary reactions to form aromatic compounds. J. Conesa et al. (1997) studied the kinetics of the decomposition of tyre wastes when heating at different rates (1, 5 and 25˚C/min) during thermogravimetric measurements. They reported that the weight loss of WT in thermobalance can be as significant as 65% (35% solid residue) and that the weight loss takes place in three steps, the first corresponding probably to the decomposition of an oil fraction, the second to that of NR and the third to SBR. They proposed a model for the weight loss from which they concluded that the first fraction defined contributes with w_{10}=0.29 (45.17% of the total weight loss), the second fraction with w_{20}=0.23 (35.885% of the weight loss) and the third fraction with w_{30}=0.121 (18.95% of the total weight loss). Moreover, they

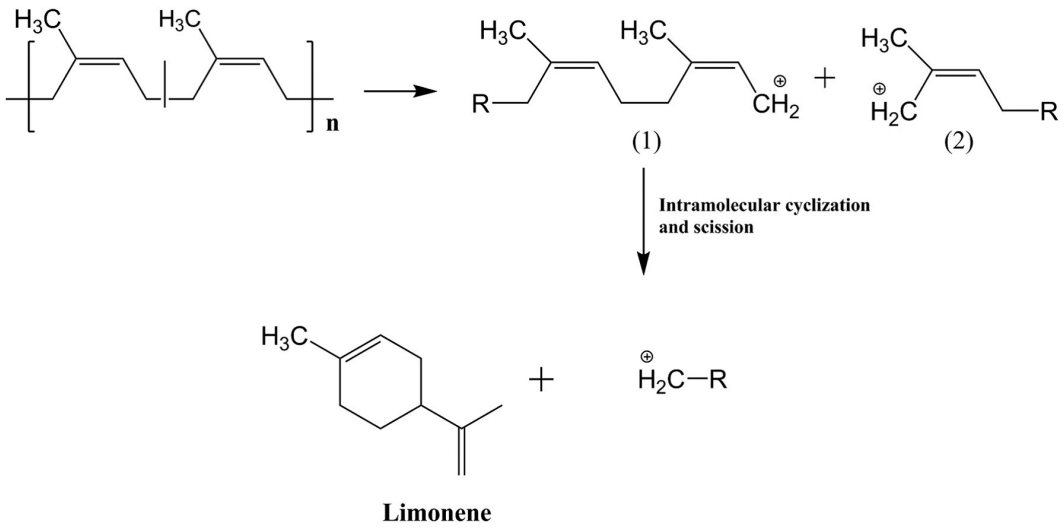

FIGURE 2: Limonene formation mechanism in tyre pyrolysis (G. Zhang et al., 2021).

observed that the first fraction that decomposes produces mainly CO_2 and linear hydrocarbons. CO_2 has also been formed in the second stage of decomposition (NR degradation), while SBR mainly produces aromatic compounds.

Quek and Balasubramanian (2009) developed a new model to provide insights into the pyrolysis kinetics of tyre by the use of an algorithm that includes two equations, one to count for heat conduction from the exterior to the interior of the tyre particle, and the other for mass transfer from within the tyre particle to the surface. They reported that the pyrolysis kinetics and the product composition and evolution are highly dependent on the heating rates maintained in the reactor. Specifically, at heating rates beyond 30 K/min, the TGA curves revealed an abrupt change in the pyrolysis process. However, the proposed model supposes that principal constituents of tyres are extender oil, NR, BR and SBR and that each of these components follows the basic Arrhenius-type equation with the first-order reaction. This model effectively described the influence of the various kinetic parameters on the pyrolysis reactions at different heating rates. Therefore, it is evident that incorporating heat and mass transfer processes in a pyrolytic model can improve the quantitative understanding of tyre pyrolysis, as was shown by the better fits of the model results at higher rates (>30 K/min). F.A. Lopez et al. (2013) determined the granulated scrap tyres (GST) thermal decomposition kinetics by TGA/DTG and compared the determined apparent activation energy and the pre-exponential factor values via the use of the Friedman, Flynn-Wall-Ozawa and Coats-Redfern model-free methods at different heating rates (5, 10, 15 and 20˚C/min). They showed that thermal decomposition starts at about 290˚C and is complete at 550˚C. The reaction begins with the dehydration and devolatilisation of the processing oils, followed by the NR and BR decomposition. The mean E_a values obtained by the different model-free methods used were similar, with an average of 160 kJ/mol and an average A of 2.49×10^{10} min^{-1}. However, as determined by the Coats-Redfern method, the thermal decomposition reaction model was accounted for by the D3 model. Moreover, the constant activation energy over the α interval (0.01-0.99) suggests that the pyrolysis of GST is a multi-step process.

Miranda et al. (2013) conducted a study of possible routes for the pyrolysis reaction mechanism of rubber tyre wastes (RT) in a micro-autoclave using an evaluation integrating both experimental data and different kinetic models. They evaluated kinetics models based on the results obtained at different temperatures (up to 350, 370, 390, 410, 430, 450˚C) and reaction times. They also established new reaction pathways involving a combination of series and parallel reactions in RT pyrolysis, as none of the mechanisms in the literature allowed the numerical adjustment to the experimental data. The authors proposed the reaction mechanisms based on: i) the physical state of the products obtained, ii) all reactions are elementary first-order and irreversible, iii) temperature dependence of the rate constants are described by the Arrhenius equation and, iv) there are no mass transfer resistances in the reaction medium.

Bart Danon and Görgens (2015) used a combined model-free and model-based kinetics employing a sophisticated devolatilisation mechanism to obtain the rubber composition of waste tyre crumbs. They predicted the rubber composition of three different WT crumbs using a kinetics model based on a sophisticated mechanism, including two consecutive devolatilisation reactions for the rubbers and a single intermediate condensed product. Using Friedman's method, the activation energies obtained were close for all the mixtures and in the range of 220 – 240 kJ/mol. These values were subsequently incorporated as fixed values in model-based kinetics, and pre-exponential factors were found to be strongly related to them, i.e., higher values of E result in higher values of A. the reaction order, however, remains around unity for lower values of E, while its value rises with higher values of E. The model was validated with binary and ternary mixtures of three predominant tyre rubbers (NR, BR and SBR) and subsequently applied for three WT crumbs consisting of different ratios of PCT and TT. The model was found capable of accurately predicting the natural polyisoprene content. B Danon et al. (2015) studied the devolatilisation behaviour of four rubbers (NR, PI, BR and SBR) by combined model-free (Friedman and Kissinger) and model-based kinetics and using a TGA-DTA instrument. They observed two distinct zones of weight loss for all four rubbers. These zones were the primary depolymerisation/condensation and the condensed product's secondary (subsequent) degradation. Moreover, data from DTG and DTA indicated that the two butadiene rubbers started to boil around 450˚C. The fixed values of the activation energy derived from the two isoconversional methods, ranging from 200 to 440 kJ/mol, were implemented as fixed values in a model-based kinetic procedure. The implementation resulted in a decrease in the degrees of freedom of the model-based multivariate nonlinear regression procedure. Therefore, the combined model-free and model-based approach was proved to accurately predict the devolatilisation of the four investigated rubbers.

3.2 Theoretical approaches

Throughout the modern history of thermal decomposition, the kinetic analysis of pyrolysis processes has gained justified interest from many investigators for two reasons (Uzun & Yaman, 2014): i) Kinetic data are crucial in designing any kind of device in which the thermal decomposition takes place, and ii) Kinetics is intrinsically related with the decomposition mechanisms. Kinetics is the starting point for postulating mechanisms for thermal decomposition.

Kinetic data from solid-state pyrolysis reactions have typically been obtained using discrete isothermal methods of analysis and is acquired by performing several experiments under isothermal conditions at different temperatures. Conversely, dynamic methods, which are performed under non-isothermal conditions, have attracted much appeal given their ability to investigate a range of temperatures expeditiously. Non-isothermal analytical techniques use modern thermobalances that subject samples to a programmed continuous temperature rise, ensuring that no temperature regions are omitted, as can occur during discrete isothermal measurements. In addition, studies have shown that there are wide disparities among values

obtained from dynamic techniques that use a single heating rate. A consensus emerged that the accuracy of these methods could be improved using multiple sets of thermal data collected by performing experiments at various heating rates (White et al., 2011).

Solid-state kinetics can be studied with thermal analytical methods by measuring a sample property as heated or held at a constant temperature. If a reaction involves weight loss, then the weight is followed throughout the reaction, and the kinetics are usually studied by thermogravimetric analysis (TGA). Heat, evolved or consumed, is another measurable property used for kinetic evaluation using differential scanning calorimetry (DSC) or differential thermal analysis (DTA). Weight loss or heat flow data are converted to a normalised form called conversion fraction (α). The conversion fraction ranges from 0 to 1 and measures reaction progress as a function of time or temperature (Khawam & Flanagan, 2006a).

3.2.1 Rate-laws

Equation 1 depicts the rate of a solid-state reaction in its most general form (Khawam & Flanagan, 2005):

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \quad (1)$$

Where k is the reaction rate constant, f(α) is the reaction model, and α is the conversion fraction.

For isothermal thermogravimetric analysis, the conversion fraction at any time is (Khawam & Flanagan, 2006a):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

Where: m_0 is the initial sample weight, m_t is the sample weight at time t, and m_∞ represents the final sample weight. Non-isothermal, the conversion fraction at any temperature is:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \quad (3)$$

Where: m_t is the sample weight at temperature T

Integrating the above equation gives the integral rate law,

$$g(\alpha) = kt \quad (4)$$

Where: g(t) is the integral degradation model.

The temperature dependence of the rate constant is described by the following Arrhenius equation,

$$k = Ae^{-E_a/RT)} \quad (5)$$

Where: A is the pre-exponential (frequency) factor, E_a is the activation energy, T is the absolute temperature, and R is the gas constant.

Substituting Equation 5 in the above rate expressions gives,

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}\, f(\alpha) \quad (6)$$

And,

$$g(\alpha) = Ae^{-E_a/RT}\, t \quad (7)$$

Equation 6 and 7 can be transformed into non-isothermal rate expressions describing reaction rates as a function of temperature and at a constant heating rate by utilising the following equation,

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\,\frac{dt}{dT} \quad (8)$$

Where: dα/dT is the non-isothermal reaction rate, dα/dt is the isothermal reaction rate, and dT/dt is the heating rate (β).

Substituting Equation 6 in the above equation gives the differential form of the non-isothermal rate law,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (9)$$

Upon integration, Equation 9 gives,

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E_a/RT}\, dT$$

If Ea/RT is replaced by "x", and the integration limits are transformed; the above equation becomes,

$$g(\alpha) = \frac{AE_a}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2}\, dx \quad (10)$$

Which is written as,

$$g(\alpha) = \frac{AE_a}{\beta R}\, p(x) \quad (11)$$

Where p(x) is the exponential integral.

The exponential integral p(x) has no analytical solution but has many approximations. Thus, the approximation of temperature integral is the key to understanding the different analysis methods (Starink, 2003). The main approaches used for evaluating the temperature/exponential integral are (Khawam & Flanagan, 2006a): i) calculating values of p(x) numerically, ii) converting p(x) to an approximate form that can be integrated and, iii) approximating p(x) by a series expansion. There are three approximations that have been used frequently over the years (Flynn, 1997; Flynn & Wall, 1966): Schlömilch Expansion, Asymptotic expansion and Expansion in a series of Bernoulli Numbers.

Thus, these asymptotic expansions are generally expressed in the form (Starink, 2003):

$$p(x) = \frac{e^{-x}}{x(w+x)}(1 + g(x)) \quad (12)$$

Where: w is a constant, g(y) is an expansion of which the first term is of the order y^{-1} or y^{-2}, with g(y)"1, providing y is more significant than about 10. By taking non-integer values of w, many more expansions can be derived. One of them is the approximation made by Senum and Yang described by the equation,

$$p(x) \cong \frac{e^{-x}}{x^2} h(x) \quad (13)$$

With h(x) is the ratio of two polynomials, its fourth-order approximation is given by,

$$h(x) = \frac{x^4 + 18x^3 + 86x^2 + 96y}{x^4 + 20x^3 + 120x^2 + 240y + 120} \quad (14)$$

This expansion is generally limited to only the first term or the first two terms for deriving p(x). Equation 15 gave the first term expansion and led to the Kissinger-Akira-Sunose method (Starink, 2003).

$$p(x) \cong \frac{e^{-x}}{x^2} \quad (15)$$

The two first terms approximation has been used by Coats and Redfern and is given by:

$$p(x) \cong \frac{e^{-x}}{x^2}\left(1 - \frac{2}{x}\right) \quad (16)$$

Doyle, however, suggested a linear approximation of the logarithm of p.

$$\log p(x) \cong -0.4567x - 2.315 \quad (17)$$

The determination of the function f(α) and the constants A and E are required for a complete description of the reaction progress at all temperatures and for all temperature-time programmes.

3.2.2 Models and mechanisms

A model is a theoretical and/or mathematical description of what is observed experimentally. In solid-state reactions, a model describes a reaction and can usually be converted into a mathematical expression, i.e., rate expression (Khawam & Flanagan, 2006a). Models are generally categorised based on the graphical shape of their isothermal curves (α vs t or dα/dt vs α) or their mechanistic assumptions. Based on their profile, kinetic models can be grouped into acceleratory, decelerator, linear, or sigmoidal models. Based on mechanistic assumptions, models are classified into nucleation, geometrical contraction, diffusion, or reaction-order (Table 2) (Khawam & Flanagan, 2006b). However, Šesták and Berggren (1971) have suggested a mathematical form that represents all models in a single general expression:

$$f(\alpha) = \alpha^m (1-\alpha)^n (-\ln(1-\alpha))^p \quad (18)$$

With m, n, and p, the constant factors

By assigning values to the three variables, any model can be expressed. The above equation has been simplified by Perez-Maqueda et al. (2006) into a simple form and was found able to describe every kinetic model just by selecting the proper c, n and m parameters:

$$f(\alpha) = c(1-\alpha)^n \alpha^m \quad (19)$$

An alternative method for determining a plausible kinetic model can be based on a modified master plot, comparing the theoretical curves with the experimental ones. The master plot is a characteristic curve independent of the measurement condition, easily obtained from experimental data and based on both the first and the second derivatives of α (Criado et al., 1989). The master plots are referenced theoretical curves depending on the kinetic model but generally independent of the kinetic parameters. As in many cases, the experimental kinetic data can easily be transformed to the experimental master plots, comparison of the theoretical master plots drawn by assuming various kinetic models with the experimental master plot allows the selection of the appropriate kinetic model of the process under investigation or, at least, of the type of proper kinetic models. This method can be applied to the kinetic analysis of solid-state reactions, whatever the type of temperature program used for recording data. A single curve is enough to construct the experimental master plots in isothermal conditions. In non-isothermal states, the knowledge of both α as a function of temperature and activation energy is required to calculate the master plot curves from the experimental data (Gotor et al., 2000).

Today, a significant step in the pyrolysis process is intensifying the use of pyrolysis reactors, for which a kinetic model must be appropriately maintained to fully describe the complexity of the processes that occur during the thermal degradation of large polymer chains (Khiari et al., 2018). A general objective of modelling thermally activated reactions is to derive a complete description of the progress of a valid reaction for any thermal treatment, be it isothermal, by linear heating or any other non-isothermal treatment (Starink, 2003).

In solid-state kinetics, mechanistic interpretations usually imply identifying a reasonable reaction model because information about individual reaction steps is often challenging to obtain. However, the choice of a reaction model requires other complementary techniques such as microscopy, spectroscopy, X-ray diffraction, etc. (Khawam & Flanagan, 2006b). Thus, the modelling of tyre pyrolysis kinetics gives an overview of the mechanisms responsible for the decomposition process and predicts the potential difficulties in the pyrolysis reactor (Khiari et al., 2018).

3.2.3 Methods for WT kinetic study

Several methods used to study solid-state kinetics are also utilised for WT pyrolysis kinetics. These methods can be generally grouped into experimental and computational categories (Khawam & Flanagan, 2006a).

Experimental methods

Isothermal and non-isothermal methods are utilised to obtain solid-state kinetic data. Isothermal methods are based on maintaining samples at several constant temperatures, and as a result, a set of α – time points are produced at each temperature. These methods are based on the isothermal rate equations (Equation 6 and 7). Non-isothermal or dynamic methods involve heating samples at constant heating rates (usually linear) and following the reaction course (Khawam & Flanagan, 2006a).

The determination of kinetic parameters by non-isothermal methods present some advantages such as i) the kinetics can be established over an entire temperature range continuously, ii) the possibility to obtain a lot of information such as temperature at maximum devolatilisation rate, characteristic temperatures, and kinetic parameters with a single sample, iii) avoidance of sample-to-sample error by using a single sample, and iv) avoid some degradation that may occur during the preheating period, mainly when the temperature of onset of reaction is considerably lower than the temperature of isothermal trials (Carrasco, 1993).

Calculation methods

Two groups of methods are used to analyse either isothermal or non-isothermal solid-state kinetic data, model-fitting and model-free methods (Khawam & Flanagan, 2006a). Several researchers have regrouped these methods into several classes depending on their derivation basis. For example, Flynn and Wall (1966) classified the different methods of kinetic analysis into five categories, i.e., integral methods utilising weight loss versus temperature data directly, differential methods using the rate of weight loss, difference-differential methods involving differences in rate, methods especially applicable to initial rates and, nonlinear or cyclic rate methods. In the same way, Carras-

TABLE 2: Solid-state rate expressions for different reaction models (Khawam and Flanagan, 2006b).

Model	Differential form $f(\alpha)=1/k\ d\alpha/dt$	Integral form $g(\alpha)=kt$
Nucleation models		
Power law (P2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law (P3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law (P4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Avrami – Erofeyev (A2)	$2(1-\alpha)\ [-ln(1-\alpha)]^{1/2}$	$[-ln(1-\alpha)]^{1/2}$
Avrami – Erofeyev (A3)	$3(1-\alpha)\ [-ln(1-\alpha)]^{2/3}$	$[-ln(1-\alpha)]^{1/3}$
Avrami – Erofeyev (A4)	$4(1-\alpha)\ [-ln(1-\alpha)]^{3/4}$	$[-ln(1-\alpha)]^{1/4}$
Prout – Tompkins (B1)	$\alpha(1-\alpha)$	$ln[\alpha/(1-\alpha)]$
Geometrical contraction models		
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting area (R3)	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Diffusion models		
1-D diffusion (D1)	$1/(2\alpha)$	α^2
2-D diffusion (D2)	$-[1/ln(1-\alpha)]$	$(1-\alpha)ln(1-\alpha)+\alpha$
3-D diffusion – Jander (D3)	$[3(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3}]$	$(1-(1-\alpha)^{1/3})^2$
Ginstling – Brounshtein (D4)	$3/[2((1-\alpha)^{-1/3}-1)]$	$1-(2/3)\alpha-(1-\alpha)^{2/3}$
Reaction-order models		
Zero-order (F0/R1)	1	α
First-order (F1)	$(1-\alpha)$	$-ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^2$	$[1/(1-\alpha)]-1$
Third-order (F3)	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2}-1]$

co (1993) classified the methods into integral, differential and special methods. They defined special methods as those that cannot be classified as integral or differential. They are generally based on detailed experimental data or need data previously evaluated from graphical plots. However, Ortega (2002)1) stated three methods used to overcome different limitations found in fitting kinetics data: i) the empirical function which is the equation of Sestak and Beerggren, ii) the master plots and, iii) the isoconversional methods.

In a non-isothermal experiment, both T and α vary simultaneously. The model-fitting approach generally fails to achieve a clean separation between the temperature dependence k(T), and the reaction model, f(α). As a result, almost any f(α) can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters. In addition, because isothermal and non-isothermal experiments are conducted in different temperature regions, if decomposition involves several steps with varying energies of activation, the contributions of these steps to the overall decomposition rate measured in the thermal analysis experiment will vary with both temperature and extent of conversion. This means that the effective activation energy determined from thermal analysis experiments will also be a function of these two variables. The usual implementation of model-fitting methods aims to extract a single value of the activation energy for an overall process. Therefore, the value obtained in such a way is an average and does not reflect changes in the reaction mechanism and kinetics as a function of temperature and the extent of conversion (Vyazovkin & Wight, 1999).

The drawbacks mentioned above of model-fitting can be avoided with the use of isoconversional methods. Firstly, these methods allow the determination of the activation energy as a function of the extent of conversion and/or temperature. Secondly, this dependence is determined without making any assumptions about the reaction model. Hence, these methods are likely to produce consistent kinetic results from isothermal and non-isothermal experiments.

Therefore, the model-free isoconversional methods emerge as an alternative to model-fitting methods for their attractive attributes that i) they can be used to analyse either isothermal or non-isothermal data, ii) results from isothermal and non-isothermal experiments are internally consistent, and iii) the explicit evaluation of E_a - α dependencies can reveal complexities in the reaction kinetics (Vyazovkin & Wight, 1999).

Table 3 (*please see the supplementary material)* presents the commonly used methods in the Kinetics study of WT pyrolysis with their characteristic equations.

It is worth noting that:

- The Coats-Redfern Method model gives entirely satisfactory results when kinetics follow a simple order(-Flynn & Wall, 1966) but presents no significant difference, at low conversion levels, between zero and first-order kinetics (Carrasco, 1993).
- The Freeman-Carroll Difference-Differential method shows some imprecisions because both the first and

the second conversion derivatives are calculated from differences between two discrete experimental points (Δf/ΔT). Moreover, due to the approximation $\frac{d^2f}{dT^2} \approx \frac{\Delta^2 f}{\Delta T^2}$, this method is, therefore, of low accuracy (Flynn & Wall, 1966).

- Friedman's method applies to data sets obtained at different heating rates β_i and/or different temperatures T_i (Venkatesh et al., 2013). However, it requires numerical differentiation of the experimental α versus T curves that typically results in quite noisy rate data and thus, unstable E_a values. This drawback is avoided by using integral isoconversional methods (Vyazovkin & Sbirrazzuoli, 2006).
- The Kissinger Method, compared to the isoconversional methods, the Kissinger method has a limitation because it produces a single value of the activation energy for the whole process. As a result, the obtained value is sound only if there is no variation of E_a with α throughout the process. Unfortunately, such variations are pretty typical, and the Kissinger method cannot detect them. Therefore, the E_a values obtained by this method should generally be treated with caution unless an isoconversional approach has demonstrated E_a to be independent of α (Vyazovkin & Sbirrazzuoli, 2006).
- Starink's method integrates the isoconversional approaches of Flynn-Wall-Ozawa and Kissinger-Akira-Sunose into a single expression. This method, applied in several kinetic studies, appears to be at least an order of magnitude more accurate than the two FWO and KAS approaches (Starink, 1996, 2003).

4. GAP IN KNOWLEDGE

The present study provides a comprehensive overview of the current knowledge regarding the pyrolysis of waste ground tyre rubber and discuss the waste ground tyre rubber kinetics mechanisms and modelling approaches, there are several areas that present gaps and require further investigation.

- Lack of consensus on parameter relationships: the study highlights the lack of agreement among different studies on the relationship between product yields and various parameters. This indicates a need for more systematic and standardized research to establish clear correlations between the operating conditions and the resulting product composition. Further investigation is necessary to determine the optimal conditions for different types of feedstock and to understand the interactions between various pyrolysis parameters.
- Limited understanding of reaction pathways: the study acknowledges that the kinetic mechanism studies on waste ground tyre rubber pyrolysis are inadequate. While there has been some focus on tracing the devolatilisation of main components, there is little of research on the formation of specific chemicals and their kinetics. Investigating the formation of important chemicals during pyrolysis, such as limonene, terpinolene, indene or p-cymene, would provide valuable insights into the reaction pathways and help optimize the process for desired products outcomes.
- Lack of scalability and economic viability assessment: while the study provides a theoretical understanding of the kinetic mechanisms underlying waste ground tyre rubber pyrolysis, there is a lack of discussion on the scalability and economic viability of the process. Assessing the feasibility of large-scale implementation, including cost analysis, energy requirements, and environmental impacts, is crucial for evaluating the practical applicability of pyrolysis as a waste management solution. Future research should focus on bridging the gap between laboratory-scale studies and real-world implementation.
- Integration of experimental and modelling approaches: the study briefly mentions the integration of the thermogravimetric analysis (TGA), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and modelling as a promising approach to understanding reaction pathways. However, there is a need for more comprehensive studies that combine experimental data with rigorous kinetic modelling techniques. Such integration would enable accurate predictions of product yields and composition under different operating conditions and aid in the optimization of the pyrolysis process.

5. CONCLUSIONS AND FUTURE PERSPECTIVE

This paper reviewed the progress in understanding mechanisms underlying the WGTR pyrolysis process. Based on various data from the literature, the WGTR pyrolysis is dependent on its operating parameters, primarily the temperature. The review included a comprehensive discussion of the effects of various parameters on product yields and properties. Several authors have initiated kinetics studies to understand the reactions pathways to design the process reactors better and increase the process's economic viability. The study presented and discussed solid-state kinetics models and methods for determining kinetic parameters. The literature has revealed that selecting the correct form of the model function and choosing the proper determination method would result in a more accurate prediction of WGTR pyrolysis mechanisms. Due to the average values of kinetic parameters obtained (E_a ranging from 101-176 $kJ.mol^{-1}$), model-fitting approaches cannot disclose the complexity of reactions in solid-state thermos analysis. The model-free isoconversional methods, on the other hand, allow unmistakably detecting multi-step kinetics dependence of the activation energy on the extent of conversion. Still, they are also subject to some uncertainties, owing to the approximations necessary for their applicability. As a result, a trend has arisen to combine the two approaches to predict mechanisms better.

Furthermore, recent studies have shown that the integration of TGA, Py-GC/MS and modelling allows for a deeper understanding of the reaction pathways that regulate WGTRs pyrolysis, laying the groundwork for future research in this field. From the literature, the thermal devol-

atilisation of the WGTRs can be characterised by devolatilisation/condensation reactions with subsequent conversion of radicals, monomers and dimers to char, volatiles and gas. Moreover, depending on the temperatures and bond energies, the process balances endothermic and exothermic reactions. The studies have shown a maximum yield of limonene and isoprene of 51% and 20.5% respectively, at temperature around 500°C. The isoprene yield has been found to increase more to up to 37.57% with the use of catalyst such as CaO.

However, the kinetic mechanism studies on the thermochemical treatment of waste tyres are inadequate and restricted due to an emphasis on profiling/tracking devolatilisation of the feedstock's main components rather than tracking the chemicals' formation such as limonene, terpinolene, indene and p-cymene. The limited information available in the literature focuses primarily on increasing DL-limonene in TDO and estimating kinetic parameters related to the formation of isoprene and DL-limonene. As a result, further research is needed to correlate the yields of significant chemicals to kinetic data and reach general agreements on the reaction pathways, thereby increasing the process's economic viability. Moreover, since the reaction routes for WGTRs pyrolysis are sensitive to the material composition, particle sizes, thermal regime (heat or kinetic control) and, thus, to the experimental system, more research into the influence of these parameters on the kinetics and selectivity to attractive fractions or chemicals will aid process design and scaling up.

WGTR pyrolysis has undergone significant industrial development in recent years, evolving from a promising concept to a mature and economically viable waste management solution. This industrial growth has been driven by a combination of environmental imperative, economic incentives, and technological advancements. The economic viability of industrial WGTR pyrolysis is a primary concern, with companies conducting feasibility studies to assess factors like feedstock availability, product marketability, and return on investment. Hence, the are ongoing research and development efforts dedicated to improving process efficiency, developing novel catalysts, and exploring innovative applications for pyrolysis products.

While the study provides valuable insights into the kinetic mechanisms underlying waste ground tyre rubber pyrolysis, there are several areas that require further investigation. Future research should focus on establishing clear correlations between operating parameters and product yields, understanding the formation of specific chemicals during pyrolysis, characterizing pyrolysis products in greater detail, assessing the scalability and economic viability of the process, and integrating experimental and modelling approaches. Addressing these gaps will contribute to the development of more efficient and sustainable waste management strategies for waste ground tyre rubber.

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