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Assessing the impacts of feedstock and process control on pyrolysis outputs for tyre recycling

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ABSTRACT

Tyres are a problematic waste stream which are associated with low recycling rates; most are dumped or incinerated, offering poor value return from this material-rich and energy intensive waste. Pyrolysis offers the potential for ~30% of a tyre to be directly recyclable as 'recovered carbon black' (RCb), potentiating tyre-to-tyre recycling. However, most attempts to exploit the process have failed to produce consistent, high quality RCb on a commercially viable scale. Current consensus implies that RCb quality can only be improved by expensive post-processing, such as demineralisation using chemical solvents. Here it is shown that the quality (ash and volatile matter content) and consistency of RCb can be improved significantly by careful application of feedstock and process control during pyrolysis. This was achieved via the analysis of peer reviewed data from 31 waste tyres and yields from 161 runs in 37 pyrolysis reactors. A statistical bootstrapping regime showed that by selective exclusion of high ash tyres, and mixing the remainder thoroughly, RCb ash content could be reduced from 49% (upper 99% CI) to 14%. By utilising a unique reactor classification, it was found that fixed beds performed inconsistently, whilst rotary kilns and conical spouted beds produced high quality RCb and a high oil yield, even at lower pyrolysis temperatures. Due to their higher throughput, this work therefore suggests that application of rotary kilns with feedstock control are the best mechanisms to produce consistent high-quality products from pyrolysis, increasing the recyclability of automotive tyres.

Abbreviations

CC	Clean Char (<1% VM)
CHNS	Carbon, hydrogen, nitrogen, and sulphur analysis
P-Char-Y	Predicted clean char yield
P-Char-Ash	Predicted clean char ash content
RCb	Recovered Carbon Black
HHT	Highest Heating Temperature during pyrolysis
TPO	Tyre Pyrolysis Oil
VM	Volatile Matter
FC	Fixed Carbon

1. Introduction

1.1. Tyre pyrolysis: mechanism and development

The production and disposal of automotive tyres is creating a significant environmental burden (Sathiskumar and Karthikeyan, 2019). Around 330 kg CO₂ Eq is emitted from the production of a single tyre

(Piotrowska et al., 2019) and in 2019, annual global tyre generation was estimated to be around 3 billion tyres (Forrest, 2014; Ruwona et al., 2019). Their demanding applications require a highly engineered design with exceptional strength, flexibility, and impact and abrasion resistance characteristics. Over 90 compounds are needed to produce a typical tyre, including several rubber formulations, filler materials (carbon blacks & silica), various metals, textile belts, zinc oxide, sulphur, accelerants and other additives (Evans and Evans, 2006; Hoyer et al., 2020).

The complex composition of tyres makes recycling particularly challenging; automotive types account for the majority of global unrecycled waste polymer products (Sienkiewicz et al., 2012), some of which have historically been combusted for energy return (Pipilikaki et al., 2005). Tyre production is very energy and resource intensive, no material and only a small proportion of the energy is recovered when a waste tyre is incinerated (Amari et al., 1999). They are also commonly fly-tipped or dumped, and these tyre-piles can present a significant fire-risk and serve as mosquito-breeding sites in warmer (tropical) climates (Jimoda, 2018; Rajesh et al., 2013). Waste tyres are not suitable

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for landfilling, a practice that is banned in many countries (EC, 1999; Forrest, 2014). In order to minimise the environmental impact of tyre production and disposal, material recovery practices must develop, preferably via a closed-loop tyre-to-tyre (circular) recycling system.

Pyrolysis is currently the only viable and scalable material recovery process for waste tyres. It is defined as the thermal decomposition of a material in an inert atmosphere, and has been used to produce charcoal for millennia (Rezaiyan and Cheremisinoff, 2005). During pyrolysis, complex and large organic molecules are fragmented into a series of smaller and simpler ones which are more amenable to recovery processes. It is particularly well-suited to chemically diverse waste materials such as tyres. During pyrolysis, tyres are energized with heat, microwaves or ultrasound in the absence of oxygen to produce volatiles (pyro-gas and oil), and char (Martínez and Puy, 2013).

Pyrolysis is a more complex and condition-sensitive process than combustion because many reactions occur simultaneously. There are several reviews describing the reaction pathways involved in the pyrolysis of tyres (Aguado et al., 2006; Groves, 1991; Kwon and Castaldi, 2009; Pakdel et al., 2001) which can be categorised into two phases. Primary pyrolysis entails the decomposition of solid-phase organics into volatiles and a solid char residue whereas secondary pyrolysis, or tar cracking, involves the further cracking of gas and oil phase organics into lower molecular weight products (Li, 2004; Martínez and Puy, 2013; Senneca et al., 1999).

The dependence of the products on pyrolysis process conditions has been described elsewhere (Martínez and Puy, 2013; Williams, 2013). The principal determinant is the highest heating temperature (HHT) (Mkhize et al., 2016), although other variables such as tyre particle size, residence time, atmospheric composition and pressure also impact product composition and yields (Akkouche, 2017; Mkhize, 2019; Parthasarathy, 2016).

Most recent reviews investigating tyre pyrolysis focus on products, with an emphasis on TPO-derived fuel (Arya et al., 2020; Dick et al., 2020; Yaqoob et al., 2021; Zhang, 2008; Jahirul et al., 2021). There has also been renewed interest in TPO-derived carbon black (Okoye et al., 2021), TPO-derived solvents (Januszewicz et al., 2020), recovered carbon black (Cardona et al., 2018; Xu et al., 2020; Dabic-Miletic et al., 2021), and tyre char-derived activated carbon (Antoniu et al., 2014; Doja et al., 2022; Jones et al., 2021; Kuśmierk et al., 2021a,b). Whilst less work investigates the impact of the reactor on the process, valuable insights into catalytic pyrolysis have been reviewed (Arabiourrutia et al., 2020). Detailed information regarding reactor design and mode of operation can also be found elsewhere (Lewandowski et al., 2019; Mkhize, 2019). By quantitatively comparing feedstock characteristics with yield data from different pyrolysis reactors, this analysis provides novel insights into how tyre pyrolysis can be optimised for producing upcoming recycled products.

1.2. Advantages, limitations, and challenges associated with tyre pyrolysis

1.2.1. Product advantages

Unlike combustion, tyre pyrolysis generates multiple products amenable to various recovery or reuse applications. Tyre-derived pyrochars contain a high proportion of components originating from carbon black compounds, which are valuable, retailing for up to \$1000/tonne (Zhang et al., 2018). They have applications in inks and as a filler in recycled polymers such as new tyres (Anjum, 2019; Zhou, 2006). Char can also be converted to activated carbon adsorbents (Amri et al., 2009), battery anodes (Li et al., 2016), or used as a catalyst in other reactions (Al-Rahbi and Williams, 2017). Tyre pyrolysis oil (TPO) contains valuable light aromatic hydrocarbons, some of which have a value of >\$1000/tonne, such as benzene, toluene, xylene, rubber monomers and limonene which can be recovered and recycled (Mkhize, 2016; Pakdel et al., 2001). The TPO can also be refined to diesel or marine-grade fuel, gases and other products in the conventional oil economy using mature petrochemical processing equipment such as the fluid-catalytic cracker

or hydro-processing units, possibly through initial mixing with conventional feedstocks (Kumaravel et al., 2016; Palos, 2021). Tyre-derived syngas has a high hydrogen content with inherent potential for use in upcoming decarbonised fuels (Elbaba et al., 2011). Pyro-oil and gas products can also be combusted for energy recovery (Martínez and Puy, 2013).

1.2.2. Process advantages

The pyrolysis of waste tyres produces a smaller volume of gas relative to combustion. Consequently, gas processing and scrubbing systems can be both smaller and serviced less frequently than an equivalent-sized combustion facility (Sinn et al., 1976). Moreover, pyrolysis does not produce or release as many contaminants as partial or whole combustion. Dioxins, dibenzofurans, NO_x, heavy metals, SO_x, and alkali metals (Zn) are either not produced, or are retained within the solid char fraction (Herlan, 1978; Malkow, 2004; Unapumnuk, 2008). The TPO has higher energy and bulk density values (>40 MJ/kg) compared to the waste tyre (~35 MJ/kg) from which it was derived (Martínez and Puy, 2013), allowing it to be combusted at a higher efficiency than whole-tyre incineration (Dick et al., 2020).

1.2.3. Environmental advantages

The primary environmental advantage of tyre pyrolysis over combustion is that >35% w/w of the steel-free tyre components can be recovered as solid char, which is carbon-rich (>80% w/w), and therefore minimises the release of primarily fossil-fuel derived carbon (from carbon black) into the atmosphere under combustion conditions. A high proportion of the carbon present in TPO is derived from natural rubber, a biomaterial derived from the tree sap of *Haviea brasiliensis*. The TPO offers opportunities to be converted into valuable linear or aromatic compounds by substituting fossil petrochemical streams via the recently suggested 'waste refinery' method (Palos et al., 2021). Further, recent research shows that there is growing interest in substituting fossil fuel-derived carbon black with biomass-derived carbon black (Chang, 2021; Fan and Fowler, 2018; Lay, 2020; Peterson, 2020), or TPO-derived carbon black (Okoye et al., 2021), although more work is required which analyses their performance in tyres (Fan et al., 2020). Similarly, combustion of the pyro-gas derived from biomass-containing tyres would result in the generation of less fossil-fuel derived CO₂ than either waste tyres or fossil fuels in conventional combustion systems (I. E.A., 2008). Thus, assuming that these technologies continue to develop and that the challenges associated with sustainable rubber tree cultivation are addressed, tyre pyrolysis offers the potential of becoming a partially negative-emissions technology (Schmidt et al., 2019) thereby facilitating the move towards a tyre lifecycle which better meets the requirements of a net-zero future (García-Freites et al., 2021). Moreover, tyre pyrolysis products (see Section 1.2.1) can be used as replacements for petroleum derived compounds, further mitigating CO₂ emissions. Unlike many traditional renewable energy sources, pyrolysis kilns also have potential to be operated in a demand-response mode, according to spot power pricing, to better meet peak energy demands. Tanks storing pyro-oil could provide an excellent energy storage solution for future decentralised energy grids.

1.2.4. Current challenges and limitations

Despite the advantages over incineration, tyre pyrolysis has limitations. At higher temperatures and longer residence times, polyaromatic hydrocarbons can form from aliphatic hydrocarbons via Diels-Alder and related reaction mechanisms thereby necessitating scrubbing in gas control systems (Pakdel et al., 2001). Additional challenges include market limitations for products, legislative barriers and the high proportion of impurities in the char, which currently limits its application in high value recycled materials (Clark et al., 1993; Martínez et al., 2021). The high-sulphur content of TPO makes it challenging to utilise, and necessitates purification before it can reach, for example, a diesel standard (Tudu et al., 2016). The largest barrier to widescale commercial

development, however, is the sensitivity of pyrolysis to process and feedstock effects, and the higher level of process control required to achieve consistent performance in comparison to an incineration facility. Product variation is therefore the primary challenge facing tyre pyrolysis operators, as it is difficult to sell a product if its quality and characteristics cannot be guaranteed. Optimisation of the waste tyre pyrolysis process is therefore crucial to the development of reliable, robust, and commercially viable facilities. This work aims to address this knowledge gap by defining the critical objectives of a tyre pyrolysis system, and through analysing published data, to provide suggestion regarding how a pyrolysis system for tyres should be configured to generate consistent and high-quality products.

1.3. Objectives of an optimised tyre pyrolysis system

The schematic of a tyre pyrolysis facility illustrated in Fig. 1a is broadly representative of those which have been recently commissioned or are at planning stage. Typically, pyro-oil and pyro-gas are combusted for energy production and the tyre-char is processed and sold as recovered carbon black (RCb), which is illustrated in Fig. 1b.

To meet commercial and environmental demands, the pyrolysis system must meet 2 objectives:

- 1) Consistently produce high quality char, with minimum volatile matter (<1%) and minimum inorganic content, thereby rendering it inherently suitable as RCb.
- 2) Operate efficiently at a low HHT thereby minimising both energy requirement and secondary pyrolysis, particularly the cracking of pyro-oil to pyro-gas.

The realisation of the first objective requires complete primary pyrolysis which, under suitable operating conditions, will allow the tyre-char to be classified as RCb and hence replace virgin carbon black as the primary filler in new tyres. This would both maximise the value of the char product and increase the recyclability of tyres via pyrolysis.

The American Society for Testing and Materials (ASTM) D36 committee has produced the first standard definition for RCb (ASTM D8178) (Koury, 2018; Martinez et al., 2021), which requires the as-made char from tyre pyrolysis (raw-RCb) to be subjected to a milling or processing stage to be classified as RCb. Hence, we have assumed that post-processing will occur, thus throughout this work the solid product from the tyre pyrolysis system is referred to as RCb. The contaminants which separate RCb from Cb can be sub-categorised into volatile matter, inorganics, and carbonaceous residues (See Fig. 1b). This investigation analyses the first two, as quantitative carbonaceous residue content is not as commonly reported, and has been the focus of other research work (Cataldo, 2020; Martinez et al., 2021; Senneca et al., 1999; Zhang, 2008).

The minimisation of secondary pyrolysis causing the cracking of TPO to pyro-gas is necessary because TPO is a preferential product to tyre-derived gas; it is much easier to handle, more energy dense, can be readily and economically stored (Gamboa et al., 2020), and may be cracked to gas at a later date (Rodríguez et al., 2020). If more gas is produced than can be consumed by subsequent energy production processes, a gas flare must be used, which wastes energy and should be avoided. Moreover, by minimising pyrolysis-associated cracking, yields of valuable and recoverable chemicals in the oil can be enhanced (Januszewicz et al., 2020). This objective can be achieved by minimising the time and temperature at which pyrolysis occurs, for example

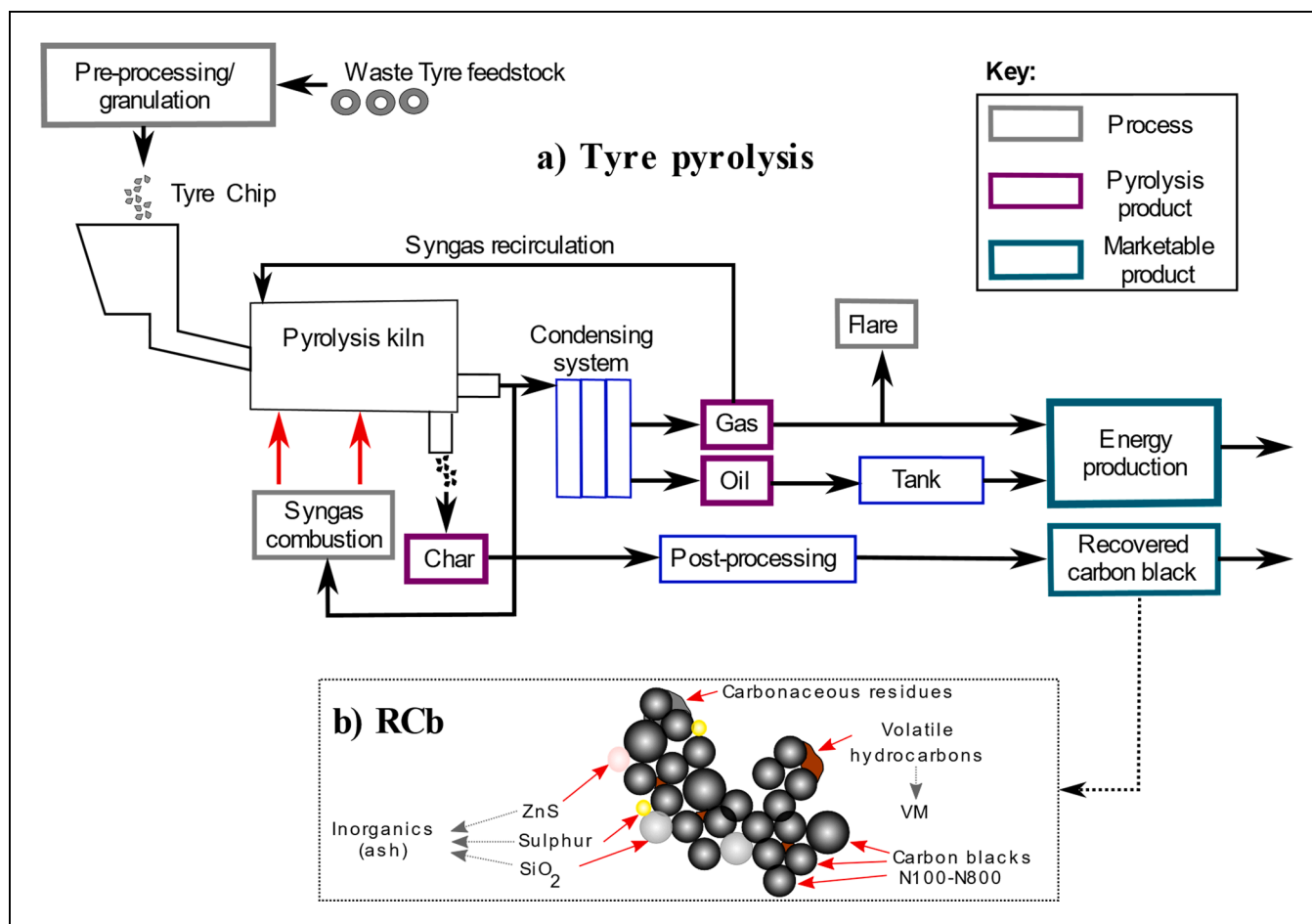


Fig. 1. a: Schematic of a tyre-pyrolysis system. 1b: Diagram of a recovered carbon black (RCb) particle.

through fast or flash pyrolysis or slow pyrolysis at lower temperatures (Lopez et al., 2017; Raj et al., 2013).

This study has quantitatively analysed over 70 published studies of tyre pyrolysis systems, with the aim of identifying the conditions which allow the two objectives described above to be optimally achieved.

2. Methodology

A schematic of the methodology used in this study is shown in Fig. 2. Criteria for the literature reviews are provided in Sections 2.1.1 (feedstock review) and 2.2.1 (reactor review). Analysis techniques are then subsequently described.

2.1. Feedstock analysis

2.1.1. Tyre feedstock characteristics

Many studies have investigated the effect of individual reactor tyre pyrolysis process conditions on the product profile. In contrast, far less attention has been paid to the waste tyre feedstock properties, which are crucial determinants of the product quality and yields. To address this limitation, proximate and carbon, hydrogen, nitrogen, and sulphur (CHNS) analyses from 31 different waste tyre samples were collected from the peer-reviewed literature and are tabulated in Appendix A. Thermal analysis data can also yield information regarding feedstock composition (NR, SBR, and textiles), and these components can influence the linear and aromatic fractions of the TPO (Athanasopoulos, 2013; Januszewicz, 2020). As proximate analysis gives a reliable predictor of approximate VM-free char yield, this information was used to inform the subsequent section analysing pyrolysis yields (See Section 2.2.1).

2.1.2. Prediction of char characteristics

The characterisation of feedstock material allows the prediction of several important determining factors in a tyre pyrolysis system. Consider the simplified equation of primary tyre pyrolysis (Eq. (1)), which can be estimated using proximate analysis data of the tyre rubber feedstock (FS) (Eq. (2)).

$$\text{Tyre rubber} \rightarrow \text{Volatiles} + \text{Char} \quad (1)$$

$$VM_{FS}, M_{FS}, FC_{FS}, Ash_{FS} \rightarrow VM_{FS}, M_{FS} + (FC_{FS}, Ash_{FS})_{CC} \quad (2)$$

where VM_{FS} , M_{FS} , FC_{FS} and Ash_{FS} refer to volatile matter, moisture, fixed carbon, and ash content from proximate analysis of waste tyre feedstock (FS) material, respectively. Following idealised separation of VM from the char, the last term of this equation (FC_{FS}, Ash_{FS}) refers to “clean RCb” (CC), i.e., containing <1% VM. The predicted yield ($P\text{-Char-}Y_{CC}$) and ash content ($P\text{-Char-}Ash_{CC}$) of the clean RCb are critical parameters in a tyre pyrolysis system and their values can be estimated from feedstock data (see Eqs. (3) and (4)).

$$P - \text{Char} - Y_{CC} = \frac{(FC_{FS} + Ash_{FS})}{(FC_{FS} + Ash_{FS} + VM_{FS} + M_{FS})} \quad (3)$$

$$P - \text{Char} - Ash_{CC} = \frac{(Ash_{FS})}{(FC_{FS} + Ash_{FS})} \quad (4)$$

This method assumes that all VM is removed from the char during pyrolysis, although in practice some VM (assumed to be <1%) remains, and there is no conversion of VM to FC. During pyrolysis some aliphatic VM will cyclise producing FC, especially at longer feedstock and volatile residence times, which are sometimes necessary to overcome slower reaction kinetics at lower pyrolysis HHT's (Martínez and Puy, 2013). Nevertheless, these processes represent a minor contribution relative to primary and secondary pyrolysis processes; hence will not be considered further. It is assumed that the sample set detailed in Appendix A is representative of waste tyre feedstock for the pyrolysis plant in Fig. 1.

2.1.3. Reduction of char ash content via feedstock controls

Bootstrapping describes any process that utilises random sampling with replacement and can circumvent assumptions regarding the shape of a population's distribution associated with traditional sampling parameters, such as the standard deviation, by assuming that the shape of the sample distribution is representative of the overall population (Mooney et al., 1993). Through this mechanism, it can predict the properties of an estimator (such as the 99% CI) of a population using a limited dataset. This was applied to the P-Char-Ash_{CC} data obtained from the method described in Section 2.1.2, to assess the effect of co-processing tyre batches on RCb ash heterogeneity. The bootstrapping method randomly sampled the tyres from the published studies which report full proximate analysis results, whilst subsequently replacing the sampled variable. A defined number of samples are taken to form the new dataset (x). The mean of the sample is calculated such that x = number of tyres from Appendix A which are co-processed. The algorithm repeats this process 100 times and produces a distribution of mean values for each x value, which is presented (Efron and Tibshirani, 1994). Due to dataset limitations ($n = 23$ with proximate analysis data), ≤ 20 tyre samples were co-processed in the analysis. Further details of the bootstrapping method are provided in Appendix C. The key assumptions of this method are: that the samples in Appendix A are representative of the feedstock available to a pyrolysis facility; that all ash is transferred to the RCb; that the tyres all have the same mass; that there is an equal chance that they are processed at any given time.

To selectively remove high-silica content feedstock from the pyrolysis analysis, data from the tyre feedstock with the highest ash yield were progressively censored. These censored datasets were then applied as input variables in the bootstrapping method outlined above to assess the combined effects of feedstock mixing and selectivity.

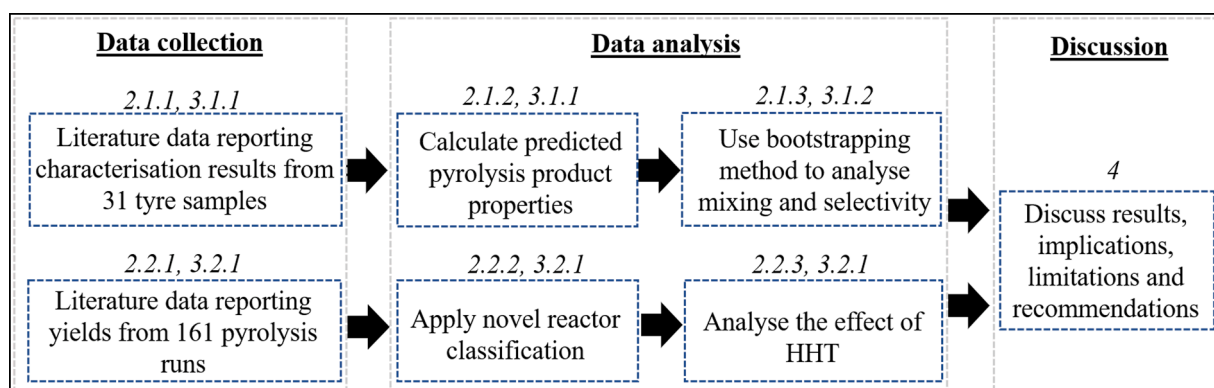


Fig. 2. Schematic of the overall methodology used in this study. References to subsequent sections are in italics.

Table 1
Pyrolysis reactor sub-classification. CAPEX = Capital expenditure. OPEX = Operating expenditure.

Pyrolysis reactor type	Reactor sub-type examples	Advantages	Disadvantages	References
Fixed bed	Single pile Layered Separate pile	- Coarse or entire tyres can be processed - Low CAPEX	- Poor OPEX: large amounts of down-time - High labour requirements - Uneven heat distribution, limited control of heating and cooling rate	(Cunliffe and Williams, 1998a; Islam, 2011; Kar, 2011; Khan, 2021; Leung and Wang, 1998; Williams et al., 1998; Williams and Brindle, 2002a,b)
Mechanically mixed bed	Rotary kiln Screw/auger kiln	- Can be continuous - Automated - No ramp up/ down - Lower OPEX - High level of control of heating rate and t_{res}	- Intermediate size granules (2–5 cm) - Possibility of blocking or seizure - Potentially poorer sealing of oxygen - Higher CAPEX than fixed beds	(Aylón, 2010; Campuzano et al., 2020; Galvagno, 2002; Proch et al., 2021; Syamsiro et al., 2019; Yazdani et al., 2019)
Fluidised bed	Bubbling bed Spouted bed Circulating bed	- Good gas sealing - Excellent heat distribution and suitable mixing - Automated - No ramp up/down - Very high level of control of heating rate and t_{res}	- Small granules required (3–15 mm), except for spouted beds - High energy demand and OPEX - Difficult to provide even mixing - Potential char losses	(Alvarez et al., 2019; Arabiourrutia, 2007; Lopez et al., 2017; Orozco, 2021; Rodríguez et al., 2019; Wang et al., 2019; Williams and Brindle, 2002b; Kaminsky and Sinn, 1980)

2.2. Pyrolysis kiln analysis

2.2.1. Tyre pyrolysis yields

A total of 161 pyrolysis runs from 37 published pyrolysis studies which reported a char, oil and gas yield were analysed. Only thermal, non-catalytic, gas-solid pyrolysis of homogenous waste tyres feedstock, processed between 450 and 650 °C, were included in the analysis. As waste feedstocks tend to have an inherently high variability, these exclusions minimised the prevalence of additional intervening variables. In addition, catalytic tyre pyrolysis was not considered as it has been subject to a recent review (Arabiourrutia et al., 2020). The minimum HHT selected for inclusion of the pyrolysis run in the analysis was 450 °C, i.e., the temperature at which tyre rubber degrades at the highest rate, as determined by differential thermogravimetry (Senneca et al., 1999). A maximum temperature of 650 °C was selected to avoid char gasification and minimise potential bias originating from a relatively small number of studies which investigated tyre pyrolysis above this temperature. The full data set is provided in Appendix B.

2.2.2. Novel reactor classification

Published studies of tyre pyrolysis are frequently characterised by a lack of data with respect to process variables such as tyre particle size, reactor conditions and operational scale. In order to address this limitation, pyrolysis reactor types were sub-categorised to facilitate elucidation of the determinants of yield (see Table 1).

2.2.3. Statistical analysis to determine effect of HHT on yields

In order to differentiate between the effects of HHT and kiln type on pyrolysis yields, published data (detailed in Appendix B) were categorised into two temperature ranges: 450–534 °C and 535–650 °C. Each dataset was then analysed with the aim of identifying significant differences with respect to kiln type.

Statistical significance ($p < 0.05$) was determined using the non-parametric two-tailed Kruskal-Wallis test. A Bonferroni correction was applied, to avoid a Type 1 error associated with multiplicity. All statistical operations were performed using inbuilt functions in MATLAB (MathWorks, USA).

Summary statistics for all graphs are presented in the supplementary information (see Appendices D, E and F). All ranges are presented as 95% CI's (calculated from 2.5% and 97.5% quantiles) unless otherwise stated.

3. Results

3.1. Tyre feedstock analysis

3.1.1. Tyre feedstock characterisation

Proximate and CHNS analyses of the tyre characterisation data are displayed as frequency histograms and box plots in Fig. 3. Median values and interquartile ranges are displayed because the parameters were not normally distributed. All parameters that were analysed displayed large variability, demonstrating a requirement for feedstock control when producing a consistent product from a heterogeneous waste stream.

The ash content of the tyres had a skewed distribution of up to 20%, which correlated inversely with FC content distribution. In contrast, the tyre C, H, N, and S contents were parametrically distributed. The C and S levels in the tyre feedstock are very high compared to other pyrolysis feedstocks (Cheah et al., 2014; Septien, 2020), with median values of 84.3% and 1.9% respectively. These would vary according to type and parts of a tyre analysed, with heavier (commercial) tyres containing higher carbon and NR contents and lighter (car) tyres containing higher SBR and potentially higher silica (ash) contents (see Appendix A). High carbon values can be associated with a high carbon-black content.

Eqs. (1) and (2) were applied to the dataset, the results of which are shown in Figs. 3i and 3j, giving indications of expected char yield and char ash content from these tyres respectively. Both showed skewed distributions and large variabilities, with a range of 23.6 to 43% for P-Char- Y_{CC} , and 6.5 to 48.9% for P-Char-Ash $_{CC}$. The P-Char- Y_{CC} had a median value of 34.3% which approximates to the char yield of a system producing clean (<1% VM) RCb. This calculated value was used in the subsequent sections as the idealised 'clean' char yield.

3.1.2. Feedstock mixing and selectivity

The results of feedstock mixing to reduce RCb ash content heterogeneity are presented in Fig. 4 and the effect of feedstock selectivity is shown in Fig. 4a-e. Fig. 4d suggests that the median P-Char-Ash $_{CC}$ value for each char sample approaches the mean (=20.8% at 100% selectivity) when mixing at least 5 tyres. The upper boundaries of the boxplots in Fig. 4a-c demonstrate the large effect exhibited by relatively few very high ash tyres (See Fig. 3j); exclusion of these results in a large reduction of RCb ash content. Further increases in tyre mixing exert a minimal effect on the median P-Char-Ash $_{CC}$.

Inorganics concentrate in the char during pyrolysis; thus, source control is a critical determinant of RCb quality, which must be

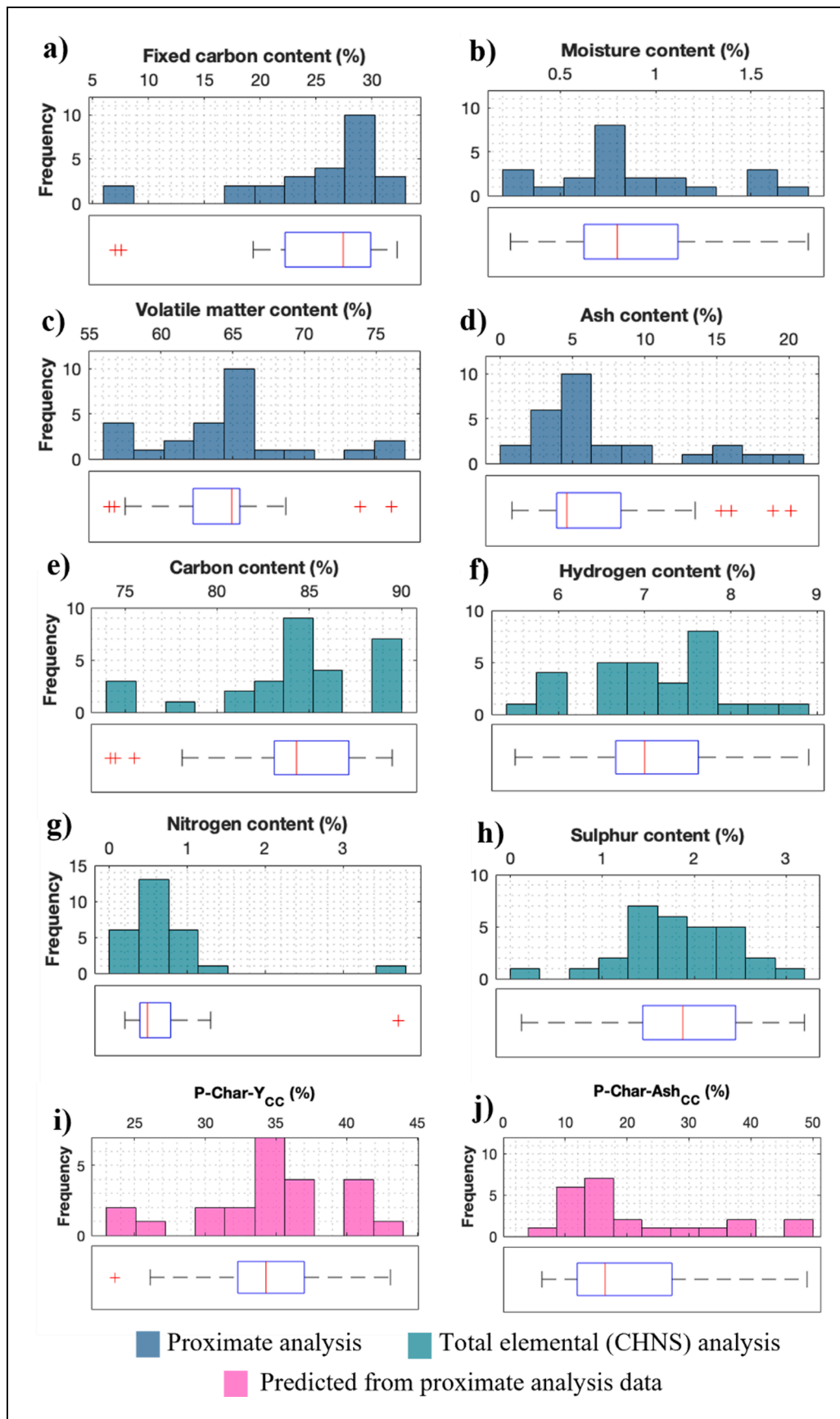


Fig. 3. Histograms and boxplots displaying proximate and CHNS elemental analysis of the steel-free waste tyre samples detailed in [Appendix A](#). Bar charts depict frequency distributions and whisker and box plots show the median, inner and outer quartiles, and outliers are shown. CHNS = Carbon, Hydrogen, Nitrogen and Sulphur.

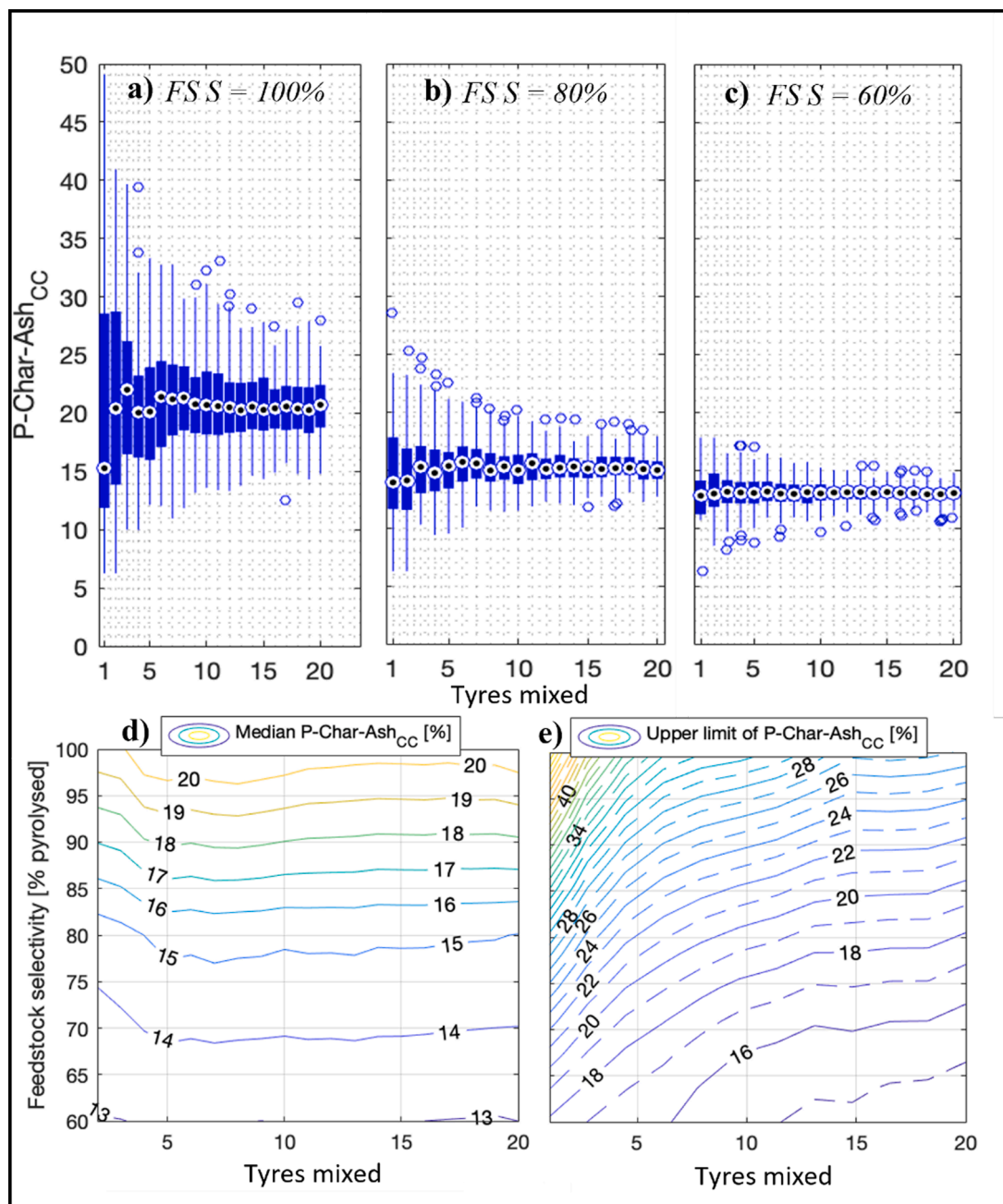


Fig. 4. a-c Boxplots showing dependence of P-Char-Ash_{CC} as a function of feedstock selectivity (FS S) and mixing: a) entire dataset ($n = 23$), b) 80% FS S ($n = 18$) and c) 60% FS S ($n = 14$). The variance of these bootstrapped distributions is presented as interquartile ranges (blue boxes) and 1.5 times the one-directional interquartile range (blue lines). Outliers are displayed as blue circles. d) Contour plot of the median value of P-Char-Ash_{CC}, when mixing and selectivity are applied (interpolated data from Fig. 4a, b and c). e) Contour showing the upper limit (the highest 1%, or 99% CI) of the P-Char-Ash_{CC} for 100 samples produced at each mixing and selectivity regime.

consistently guaranteed before RCb can be applied into higher value polymers such as tyres as a recycled product. The P-Char-Ash_{CC} variability can be greatly reduced by increasing the number of tyres in a given volume of feedstock (Fig. 4e). The contour plot illustrates that P-Char-Ash_{CC} variability similarly reduces with increasing tyre numbers, even for modestly sized tyre batches. If 15 tyre samples are mixed, the upper 99% CI limit reduces from 49% to 28%. This variability can be further reduced by adding feed selectivity (Fig. 4b-e). The tyre char ash content was reduced from $20.8 \pm 30\%$ to $15.5 \pm 2.5\%$ by removing 20% of high silica tyres from the process stream. The ash was reduced further to $13.0\% \pm 1.0\%$ after removal of 40% of high silica tyres and increasing the number of tyres mixed to 20. This illustrates that although waste tyre characteristics vary widely, only a relatively small number of high-ash

tyres are responsible for the high and variable RCb ash content. Identification and exclusion of these tyres, accompanied by thorough mixing, can significantly improve the quality and consistency of RCb. In addition, it could also reduce the variability in any possible catalytic effects from inorganics which may alter other pyrolysis product characteristics.

3.2. Tyre pyrolysis yields

3.2.1. Kiln yield analysis

Fig. 5 shows the relationship between oil and char yield for the 161 pyrolysis runs detailed in Appendix B. Average oil yield reaches a maximum of 49% at a char yield of 34%, which is similar to the average P-Char-Y_{CC} (34.4%) as determined from feedstock proximate analysis (see

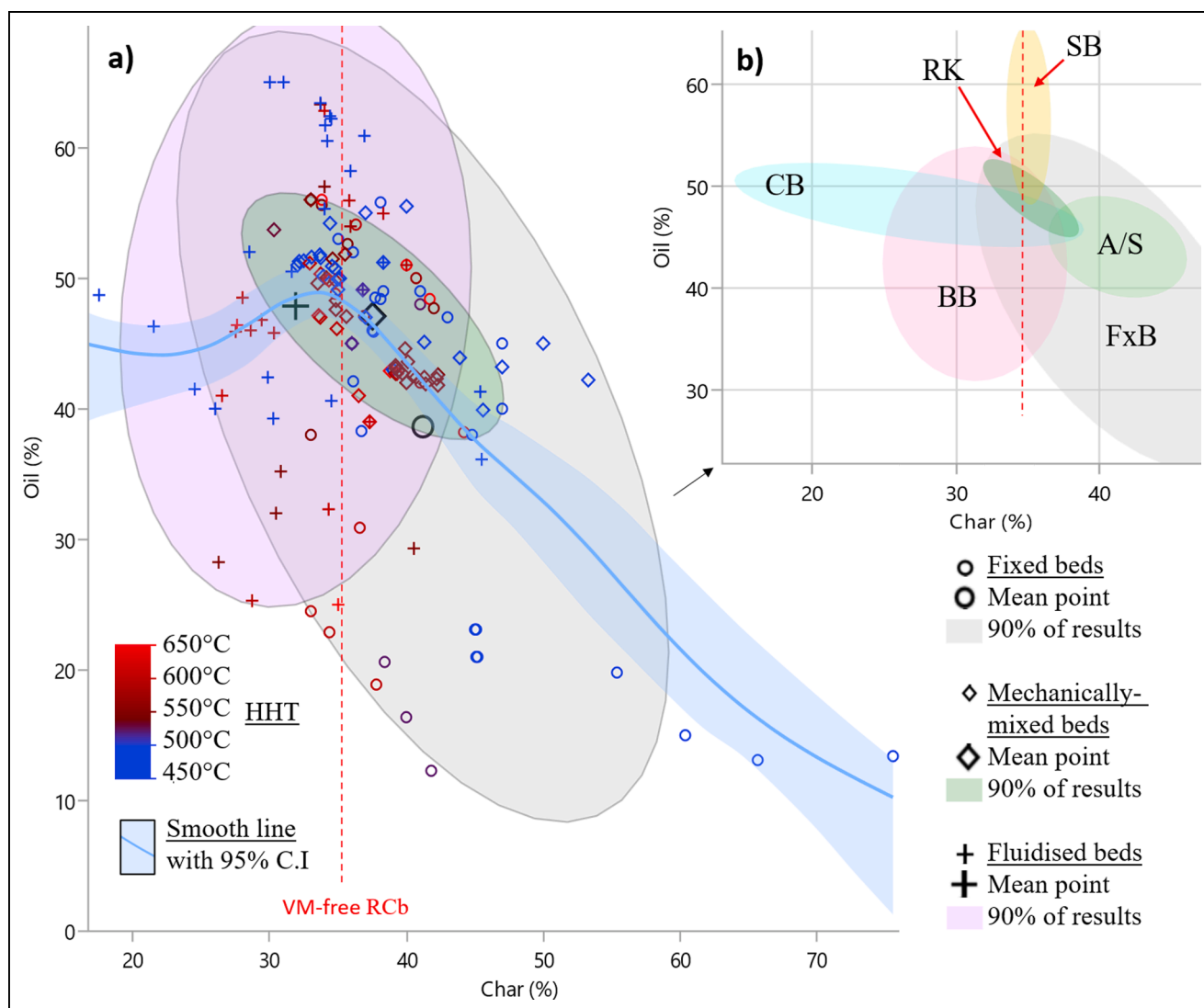


Fig. 5. a) Scatter graph showing the relationship between oil and char yield (%) for 161 pyrolysis runs in 3 kiln types: fixed bed (open circles, $n = 47$); mechanically mixed (open diamonds, $n = 61$); and fluidised bed (crosses, $n = 53$). Large black symbols correspond to mean values for each kiln type. For each pyrolysis run, the HHT is depicted according to the temperature contour. A best fit curve has been plotted from aggregate data with 95% confidence intervals (depicted in blue). Sub-division by kiln type has been applied, with ellipses showing 90% of the pyrolysis yield result, split by each reactor type. b) 50% of data enclosed in ellipses for reactor sub-type; BB = bubbling beds, CB = circulating fluidised beds, A/S = augers/screws, RK = rotary kilns, SB = spouted beds.

Section 3.1.1, Fig. 3i for details). Higher char yields (i.e., data points to the right of the red dashed line in Fig. 5) are likely to be associated with enhanced levels of residual VM, indicating that incomplete pyrolysis has occurred. Fig. 5a also shows the influence of kiln type on oil and char yields; for each kiln type, 90% of data is enclosed within an ellipse. Fig. 5b shows 50% of data enclosed within an ellipse for each reactor sub-type.

The median char yield for fixed beds (38.4%) is 1.9% higher than that of mechanically mixed kilns and 4.7% higher than fluidised bed kilns. Ranges in reported char yields were lower for mechanically mixed systems (32.0–49.9%) than in fixed (33.0–68.9%) or fluidised (17.0–45.4%) bed pyrolysis kilns. Fixed bed pyrolysis runs operated at elevated HHT's result in lower char yields, but in most cases, not higher oil yields. Some fluidised bed systems (circulating and bubbling beds) are associated with char yields of 15 to 25%, which are much lower than the predicted VM-free char yield of 34.4%. This lower char yield may be due to attrition effects resulting from the generation of aerated dust during pyrolysis within a fluidised bed, or flash pyrolysis producing more oil and gas. Conical spouted fluidised beds produce a less variable char yield, around 34–35%, showing that these reactors do not suffer from the same effects as other fluidised beds reactors. Mechanically mixed kilns produced a

char yield of 32.5 to 49.9%, with a median of 36.5%, which falls within the yields from fixed or fluidised bed designs. Auger-based kilns produced higher char yields than rotary kilns, possibly due to lower pyro-gas circulation from a relatively smaller void space within the kiln, preventing volatilisation or promoting recondensation of tar-like compounds on to the pyrolysing rubber (Cunliffe and Williams, 1998).

The large variability in oil yields throughout Fig. 5 suggest that char yield is not the only determinant affecting the extent of secondary tar cracking to pyro-gases during pyrolysis. Oil yields are broadly similar in mechanically mixed and fluidised beds (~47%), but significantly lower in fixed beds (38.6%). Ranges in oil yields were lower in mechanically mixed systems (39.9–55.5%) when compared to fluidised (25.2–65.0%) or fixed (12.8–56.0%) bed systems. All reactor types analysed showed potential for producing high (>45%) oil yields. However, only three (circulating fluidised beds, conical spouted beds, and rotary kilns) consistently produced high oil yields of above 40%. Fixed beds were commonly associated with very low oil yields, therefore producing high quantities of gas from excessive secondary cracking of pyrolysis oils, potentially wasting energy and liquid-based products. This may be due to increased HHT's, higher isothermal residence times, or lower heating rates required to achieve

adequate volatilisation and reach a given char yield. These may also cause more carbonaceous residue to deposit onto RCb, contributing to the high char yields reported from fixed beds. This suggests that heat transfer pathways are ineffective at fulfilling the objectives outlined in Section 1.3. Most bubbling beds produced high oil yields of >40% w/w, with only some results from two research groups reporting lower yields (Kaminsky, 1993; Raj et al., 2013). This suggests that high oil yields and VM-free RCb can be derived from these reactors with an optimised configuration. Conical spouted beds report very high (>60%) oil yields, possibly due to very short volatile residence times therefore reducing the potential for secondary cracking of TPO to pyro-gas, and should be subjected to further investigation. Rotary kilns, although showing a lower oil yield (45%), are a mature technology, with a higher potential throughput and a lower OPEX than spouted beds. In addition, they are less likely to suffer from tribological effects upon the reactor components from fluidised silica particles released during pyrolysis.

Reactor types differ in their heat transfer pathways due to differences in feedstock processing and mixing, hence performance variability should become more evident at lower HHT's where thermal energy is not provided in excess. Differences in the yields reported in Fig. 5 were statistically tested using the Kruskal-Wallis technique. The null hypothesis that "there is no significant difference in char and oil yields at temperatures of 450–534 °C and 535–650 °C between fixed, mechanically mixed and fluidised bed kilns" was tested. The test results in Fig. 6 and the p-values in Table 2 suggest that kiln selection is a significant determinant of pyrolysis yields at lower HHTs (450–534 °C), particularly when comparing yields from fixed beds with mechanically mixed and fluidised beds. All comparisons showed significant differences at this lower temperature, except for oil yield from mechanically mixed and fluidised bed kilns. This supports previous analysis that suggested, after HHT, reactor geometry and design have significant effects upon tyre pyrolysis outputs (Martínez and Murillo, 2013; Martínez and Puy, 2013). At the higher temperature range, the only significant difference observed was for char yields which were significantly lower for fluidised beds than the other kiln types, likely due to the aforementioned char attrition effect. This shows that poor consideration of kiln design would require a higher HHT to volatilise heavier tar components, causing detriment to the energy efficiency and oil yields of a tyre pyrolysis facility.

4. Discussion

4.1. RCb as a recycled product

Pyrolysis is the first scalable technology which may potentiate commercial scale recycling of high value products, such as RCb, from waste tyres. RCb is a composite material containing contaminants such as VM, ash and carbonaceous residues, currently too abundantly to

Table 2

Comparison of tyre pyrolysis yields between three kiln technology types. p-values of the two-tailed Bonferroni-corrected Kruskal-Wallis test are shown. Bold italicised values indicate significant differences between reactor types.

		Char	Oil
450–534 °C	Fixed vs mechanical	<i>0.001</i>	<i>0</i>
	Mechanical vs fluid	<i>0.013</i>	1
	Fixed vs fluid	<i>0</i>	<i>0</i>
535–650 °C	Fixed vs mechanical	1	1
	Mechanical vs fluid	<i>0</i>	1
	Fixed vs fluid	<i>0.001</i>	1

facilitate wide-scale deployment into recycled polymers such as tyre rubber (Norris et al., 2014). These contaminants reduce the effective surface area available for rebonding when RCb is applied as a recycled filler to new materials, thereby compromising strength, flexibility and abrasion resistance properties (Fan et al., 2020; Norris et al., 2014). Inconsistency is often a more important limitation to RCb application than quality, and so minimisation of contaminant variability in RCb is important (Moulin, 2017; Murphy and Bolder, 2020) as this has contributed to several tyre pyrolysis business failures (TRR, 2021; RJA 2020).

Silica based tyre fillers are problematic for pyrolysis by directly contributing to the RCb ash content, but they reduce rolling resistance and are not fossil-fuel derived, so are replacing carbon black in tyres in increasing proportions (Fan et al., 2020). RCb ash content is directly proportional to feedstock inorganic content, unless demineralisation techniques are applied after pyrolysis (Ahmed, 2019; Bernardo, 2012; Chaala et al., 1996; Martínez, 2019; Ucar, 2005). Despite much recent work, these demineralisation methods remain expensive, increasing the cost of RCb by \$200–400/tonne (Fleck, 2021). The acids and solvents required can cause corrosion, produce toxic gases, need stringent health and safety control systems, and can produce hazardous chemical wastes (Chaala et al., 1996; Chan et al., 2011; Martínez, 2019). This causes detriment to the economic and environmental credentials of RCb as a recycled product.

An alternative and potentially more cost-effective mechanism to reduce RCb-ash content by feedstock control is proposed (see Section 3.1.1). Excluding one-third of the highest silica tyres and mixing char from at least 20 tyres thoroughly was found to consistently produce RCb with ash contents of <14% (99% CI), facilitating incorporation into higher value products. This requires the inorganic content of each tyre to be made more accessible to pyrolysis operators, possibly through regulation, and particularly as silica-based fillers are being added to tyres in increasing proportions (Fan et al., 2020). The rejected feedstock material can be processed separately to produce a sub-tyre grade RCb via pyrolysis, used as a catalyst (Al-Rahbi and Williams, 2017),

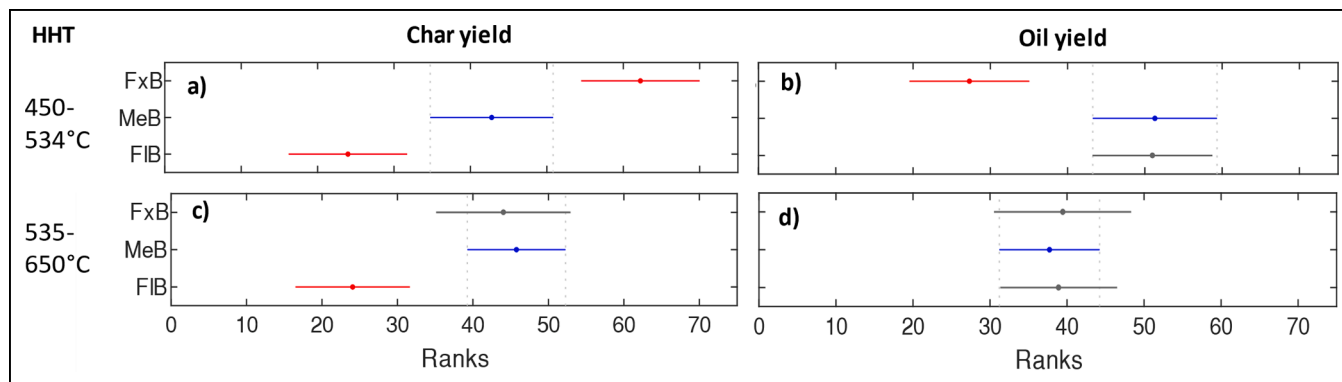


Fig. 6. Multiple comparison of Bonferroni-corrected ranks as determined by the Kruskal-Wallis test. a) char yield at 450–534 °C, b) oil yield at 450–534 °C, c) char yield at 535–650 °C, d) oil yield at 535–650 °C. The blue line indicated the group being compared (mechanically mixed kilns). Red lines show groups that are significantly different from mechanically mixed systems. Grey lines show groups that are insignificantly different from mechanically mixed systems. The circles define mean ranks. $\alpha = 5\%$.

manufactured to activated carbon (San Miguel et al., 1998, 2002, 2003), or used as fuel substitute in cement kilns (Chinyama, 2011). Alternatively, if the kiln has an air or oxygen inlet, they can be gasified to produce waste-derived syngas fuel (Oboirien and North, 2017). Future legislation should recognise that inorganic tyre-fillers can inhibit recycling via pyrolysis, and thus encourage the preferential use of bio-organic fillers, such as coconut shell derived carbons (Fan et al., 2020), over inorganic alternatives. These bio-fillers would either break down during pyrolysis or be retained as fixed carbon, and unlike inorganic fillers, would not cause significant detriment to RCb recyclability.

Waste feedstocks are heterogenous, and this study has shown that a mixing step is required to produce consistent products from tyre pyrolysis. Processing small granulate may allow for effective mixing, however, excessively small granules may promote the formation of dust. This material risks becoming entrained in the gas or TPO, or experience excessive heating rates, increasing secondary pyrolysis reactions. Due to the fact that particle size has an important influence upon pyrolysis kinetics, it must be carefully considered for a given system (Oyedun et al., 2012) and has not been analysed here.

4.2. Effective volatilisation during pyrolysis

Unlike ash content, the VM content of RCb is a function of the pyrolysis system to which it has been subject (Martínez and Puy, 2013; Martínez et al., 2013). Most studies investigating tyre pyrolysis reaction kinetics utilise thermogravimetric mass-loss or DTG data, either under a constant heating regime (Aguado et al., 2005; Aylón, 2005; Cheung, 2011; Leung and Wang, 1998; Mkhize, 2019; Wang et al., 2020) or a dynamic heating regime (Al-Salem et al., 2009; Aslan et al., 2017). Comparisons of TGA data with analysis from bench-scale pyrolysis systems are also available (Arabiourrutia, 2019; Aylón, 2005; Miranda et al., 2013), with some investigations utilising other techniques such as TGA-MS (Mkhize et al., 2019) and Py-GCMS (Menaes et al., 2020) to analyse tyre pyrolysis kinetics. These studies, however, often assume perfect or near-perfect heat transfer within a pyrolysis system. Heat transfer should be considered carefully, along with reaction kinetics, especially in larger commercial systems with fast heating rates. Eq. (5) enables the VM of a unit of RCb to be defined per unit of feedstock:

$$RCb_{VM} = FS_{VM} - \left(\frac{dX_v}{dt} \times T \right) \quad (5)$$

Where: RCb_{VM} = the volatile matter content of an RCb produced from tyre pyrolysis; X_v = volatiles liberated from char at a given temperature; and T = temperature. The rate of volatilisation in a tyre pyrolysis system can be defined by Eq. (6).

$$\frac{dX_v}{dt} = k_v(X_\infty X_n) \quad (6)$$

Where: X_∞ = the maximum fraction of a tyre which can be pyrolysed at a corresponding temperature; k_v = the kinetic constant corresponding to the formation of volatiles, and X_n is the ratio of actual conversion for a specific tyre pyrolysis system. Volatilisation in rubber comprises of gas (g), liquid linear (l), aromatic (a) and tar (t) formation, as shown in Eq. (7) (Arabiourrutia et al., 2019).

$$\frac{dX_v}{dt} = (k_g + k_l + k_a + k_t)(X_\infty X_n) \quad (7)$$

k_g can be further sub-categorised as: k_{pg} , defining primary pyrolysis gases that form directly from rubber with no liquid intermediate; and k_{sg} , which form as a result of secondary pyrolysis of liquid linear, aromatic, and tar products. The rate of change in oil yield at a specific pyrolysis temperature (dX_o) can therefore be defined by Eq. (8).

$$\frac{dX_o}{dt} = \frac{dX_l}{dt} + \frac{dX_a}{dt} + \frac{dX_t}{dt} - \frac{dX_{sg}}{dt} \quad (8)$$

Different pyrolysis reactors and rubber geometries will provide differing degrees of heat transfer, and as heat transfer becomes more perfect, X_n approaches 1. X_n can be related to the pressure (P), mixing rate (M), atmosphere (A), and particle geometries (G) of the specific tyre pyrolysis system (see Eq. (9)).

$$X_n = f(P, M, A, G, \dots) \quad (9)$$

These terms can be simplified to the maximum heat transfer pathway (MHTP), which defines the part of the pyrolysing rubber furthest from the heat source, with the least contact with the gas phase. Reactors with a low X_n value will therefore require more energy to achieve complete pyrolysis, through increasing HHT or isothermal residence time, or decreasing heating rate. Whilst there are too many unaccounted variables within the tyre pyrolysis yields between reported studies, to allow for quantitative derivation of these terms, the results presented here allow for qualitative comparisons of X_n and MHTP's between major reactor types. Both fluidised beds and mechanically mixed beds produced an average char yield close to 34%, showing that such systems are more likely to produce RCb with a low VM content (See Section 3.2.1). This can be explained by enhanced heat transfer characteristics associated with mixed kilns, providing evidence that X_n values are higher (See Eq. (10)).

$$X_n^{FIB} > X_n^{MeB} > X_n^{FsB} \quad (10)$$

Reactors with lower X_n values require higher amounts of energy (i.e., HHT or residence time) to generate VM-free RCb. This negatively affects efficiency and causes detriment to oil yields via secondary pyrolysis, explaining the low oil yields of many fixed bed pyrolysis runs. Excessive tyre pyrolysis HHT's and residence times, and low heating rates, have also been associated with carbonaceous residue deposition on the char, resulting from cyclisation and recombination reactions, negatively affecting RCb performance (Cataldo, 2020; Martinez et al., 2021; Roy, 1997; Xiang et al., 2020; Yang et al., 1995). Mechanically mixed kilns produced the least inter-pyrolysis run char yield variability, followed by fluidised beds and fixed beds (See Eq. (11)).

$$Var(X_n^{FsB}) > Var(X_n^{FIB}) > Var(X_n^{MeB}) \quad (11)$$

This suggests that mechanically mixed systems, especially rotary kilns, reliably display efficient heat transfer and are less sensitive to intervening variables such as gas flow, feedstock heterogeneity, and particle size, than fluidised systems (Li et al., 2004). Augers displayed higher char yields and lower oil yields than rotary kilns, suggesting that tar-phase compounds remain on the char after pyrolysis, possibly due to reduced gas circulation within auger based systems. Further, augers may offer more solid surface areas for the tar compounds to nucleate upon (Cunliffe and Williams, 1998; Islam et al., 2008). Although some fluidised beds have displayed remarkable heat transfer properties with exceptionally high heating rates, resulting in very high oil yields, these systems are sensitive to intervening variables such as fluidisation media composition (Alvarez et al., 2017; Arabiourrutia, 2007; Karatas, 2013; López, 2010; Lopez, 2010), gas-fluidised phase reactivity (Pecho et al., 2008), and spatial mixing heterogeneities (Karatas et al., 2013), which may not be present in mechanical systems.

Bubbling beds, circulating fluidised beds, and pneumatic transport reactors all exhibit differing gas/solid velocities and therefore would exhibit varying degrees of mixing (Lewandowski et al., 2019). By keeping fluid speeds above the minimum but below the terminal fluidisation velocity, bubbling bed reactors can generate consistent product outputs in biomass feedstocks, which may also be the case for tyre pyrolysis (Butler et al., 2011). However, bubbling beds are sensitive to particle agglomeration which risks localised overheating, a significant issue for pyrolysing rubber due to its adhesive nature, explaining some low oil yields reported from these reactors. Recent evidence has suggested that innovations such as conical spouted bed reactors create improved processing conditions for pyrolysing rubber with a lower risk

of blockage whilst maintaining a high heating rate, explaining the exceptional TPO yields reported from these systems (López, 2010; Lopez et al., 2017). Catalytic mediums, such as steam, can also be introduced to fluidised beds which may allow tyre pyrolysis to occur at a lower temperature (Elbaba and Williams, 2012). These innovations require further investigation.

5. Conclusions

- End of life tyre material recovery via pyrolysis is not being effectively achieved, due to significant limitations in methodologies currently applied such as inadequate feedstock control, lack of substrate mixing, and excessive HHT. These cause significant detriment to the quality and consistency of RCb and TPO.
- Comparative analysis of characterisation data from 31 waste tyre samples and yields from 161 tyre pyrolysis runs from 37 kilns has been conducted to assess the causes of variability and undesirable effects during tyre pyrolysis.
- The highly variable nature of tyre feedstock composition resulted in skewed distributions of key variables that affect pyrolysis product quality, such as FC, ash and VM content, with a relatively small number of tyres displaying high ash content, negatively affecting RCb quality.
- Bootstrapping quantitatively showed that excluding these high-silica tyres, along with thorough mixing of the preferred bulk tyre materials, was found to positively benefit the RCb, reducing the upper limit (99% CI) of ash content from 49% to 14% depending on the level of mixing and exclusion applied during the pyrolysis process. High-silica tyres could then be pyrolysed separately, combusted, or gasified to exploit their energy content.

- Results indicated that the consistent removal of VM from the char is likely to be best achieved using a rotary kiln or conical spouted bed at a lower HHT (450–534 °C). Such systems also consistently produce significantly higher oil yields, especially compared to non-mixed systems ($p < 0.01$).
- Key recommendations from this work are to deploy feedstock mixing and selectivity within a large well mixed rotary kiln or conical spouted bed during tyre pyrolysis. Ash contents of tyres should be made more available to tyre pyrolysis operators, possibly from regulation, so feedstock control can occur. This will allow higher quality products to be recycled from automotive tyres which will valorise and increase the sustainability of this global waste stream.

CRedit authorship contribution statement

A.J. Bowles: Conceptualization, Methodology, Data curation, Visualization, Writing – original draft. **G.D. Fowler:** Supervision, Writing – review & editing.

Declaration of Competing Interest

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

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Appendix A. Literature review showing proximate and total elemental analysis results of waste tyres. FC = feedstock, C = carbon, H = hydrogen, N = nitrogen, S = sulphur, O = oxygen. FC = fixed carbon, VM = volatile matter, M = moisture. WT = Waste tyres, WTT = Waste truck tyres, WMT = waste motorcycle tyres, WCT = waste car tyres, LWT = light waste tyre, HWT = heavy waste tyre

FS	C	H	N	S	O	Ash	FC	VM	M	Ref
WTT	84.3	7.7	0.8	2.5	4.7	4.9	29.9	65.1	0.6	(Alvarez et al., 2017)
WT	89.5	7.3		1.9		0.8				(Díez et al., 2005)
WT	83.8	7.3	1.3	2.45	4.7	2	30.02	66.46	0.7	(Antoniou and Zabaniotou, 2015)
WT	84.08	6.71	0.49	1.51	1.73	4.35	32.28	62.24	1.14	(Ghose and Isayev, 2003)
WT	84.35	6.7	0.39	1.1		3.8	31.8	63.6	0.8	(Martínez et al., 2013)
WT	81.72	6.54	0.55	1.87		6.64		62.58	0.71	(Aylón et al., 2010)
WT	83.2	8.9	0.3	1.6	6	4.6	29.7	65	0.7	(Frigo et al., 2014)
WT						7.6	7.6			(Black and Brown, 1992)
WT						7	7			(Black and Brown, 1992)
WT	83.34	6.56	0.79	1.33	2.78	4.2	32	63.04	0.76	(Li et al., 2016)
WT	78.1	8.3	0.4	3.2	10	18.9	22.24	57.81	1.05	(Yang and Ani, 2016)
WT	89.3	5.8	0.4	2.5	2	4.2	19.4	76.1	0.3	(Choi et al., 2016)
WT	86.46	7.66	0.44	2.14		3.19				(Lopez et al., 2010)
WT	82.8	7.6	0.5	1.3	4.5	3.3	27.2	68.7	0.8	(Dai et al., 2001)
WT	89.2	7.7	0.5	2.6		4.3	21.8	73.9		(Choi et al., 2014)
WT	89.4	7	0.2	2		3.7	29.4	65.5	0.9	(Conesa et al., 2008)
WT	83.92	6.83	0.78	0.92		4.16	30.08	64.97	0.75	(Zhang et al., 2008)
WT	81.1	6.81	3.71	2.07						(Muenpol and Jitkarnka, 2016)
WT	74.5	6	0.5	1.5	3					(Qu et al., 2006)
WT	85.6	7.5	0.6	2.2	1.2	2.9		65.1		(Ahoor and Zandi-Atashbar, 2014)
WT	85.52	6.94	0.47	1.7	8.37	9.63	24.08	65.45	0.84	(Banar et al., 2015)
WT	85	5.5	0.21	1.2	8.09	16	27.1	56.4	0.5	(Osayi et al., 2018)
WT				2.6		8.66	28.47	62.63	0.24	(Uyumaz et al., 2019)
WT	89.3	5.8	0.4	2.5	2	4.2	19.4	76.1	0.3	(Choi et al., 2016)
WT	86.39	6.91	0.46	0.12	1.42	4.7	29.54	64.91	0.85	(Raj et al., 2013)
WMT	75.5	6.75	0.81	1.44	15.5	20.12	20.85	57.5	1.53	(Islam et al., 2008)
WCT							29.4	62.2	1.3	(Boxiong et al., 2007)
WCT	74.2	5.8	0.3	1.5	4.7	13.5	27.7	58.8		(de Marco Rodriguez et al., 2001)
WCT	84.5	7.4		1.7						(Düng et al., 2009)
WMT	89.48	7.61	0.27	1.88	0.76	15.32	26.43	56.72	1.53	(Singh et al., 2018)
LWT	84.2	7.9	1	1.4	5.5	7.4	26.3	64.5	1.8	(Singh et al., 2018)
HWT	89.5	7.5	0.25	2.09	0.66	5.67	24.3	68.43	1.6	(Singh et al., 2018)

Appendix B. Literature review of oil, gas, and char yields from pyrolysis. FS = feedstock. PS = feedstock particle size. SM = sample mass. RT = reactor type. RST = Reactor sub-type. HHT =pyrolysis highest heating temperature. Ti = retention time at highest heating temperature FxB = fixed bed, MeB = mechanically mixed bed, FiB = fixed bed. RK = rotary kiln. ABR = ablative reactor. A/S = Auger/screw. SpB = Spouted bed. BB = Bubbling bed. CFIB = Continuous fluidised bed

RT	RST	FS	PS (mm)	SM (g)	HHT (°C)	Ti (min)	Char (%)	Oil (%)	Gas (%)	Ref
FxB	FxB	WT	5	18	465	120	45	23.1	31.90	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB	WMT	2.5		475	50	41	49	10	(Islam et al., 2008)
FxB	FxB	WT	5	18	475	30	55.4	19.8	24.80	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB	WT	20	18	475	30	75.6	13.4	21.00	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB	WT	20	18	475	30	65.7	13.1	21.20	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB	WT	20	18	475	120	45.1	23.1	31.80	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB	WT	5	18	475	120	45.1	21	33.90	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB	WT	20	18	475	120	45.2	21	32.90	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB	WT	5	18	475	30	60.4	15	24.6	(Ahoor and Zandi-Atashbar, 2014)
FxB	FxB		110	180,000	485		39	43	5	(Roy et al., 1999)
FxB	FxB	WCT	9	20	500	30	36.09	51.98	11.92	(Boxiong et al., 2007)
FxB	FxB	WCT	9	20	500	30	37.59	45.9	16.5	(Boxiong et al., 2007)
FxB	FxB	WT	3	200	500	60	38.1	55.8	6.1	(Williams and Brindle, 2002)
FxB	FxB	TT/BT	100	35,000	500	180	37.7	48.5	13.8	(Aziz et al., 2017)
FxB	FxB	TT/BT	100	33,000	500	210	38.1	48.4	15.3	(Aziz et al., 2017)
FxB	FxB	TT/BT	100	30,000	500	185	38.3	49	12.7	(Aziz et al., 2017)
FxB	FxB	TT/BT	100	32,000	500	180	37.5	46	16.5	(Aziz et al., 2017)
FxB	FxB	TT/BT			500		35	53	17	(Aziz et al., 2017)
FxB	FxB	WT	1.5		500	120	36.7	38.29	22.59	(Choi et al., 2014)
FxB	FxB	WCT		175	500	30	44.8	38	17.2	(de Marco Rodriguez et al., 2001)
FxB	FxB	WT	0.35	100	500		36.1	42.1	21.8	(Zhang et al., 2008)
FxB	FxB	WCT	0.7	30	500	60	47	45	11	(Düng et al., 2009)
FxB	FxB	WT		10	500		47	40	13	(Witpathomwong et al., 2011)
FxB	FxB	WT	1.2		500	120	43	47	12	(Muenpol and Jitkarnka, 2016)
FxB	FxB		110	158,000	520		36	45	6	(Roy et al., 1999)
FxB	FxB	WMT	5		525	50	41	48	13	(Islam et al., 2008)
FxB	FxB	WT	2	10	525		41.81	12.28	45.91	(Osayi et al., 2018)
FxB	FxB	WT	2	10	525		39.98	16.38	43.64	(Osayi et al., 2018)
FxB	FxB	WT	2	10	525		38.4	20.61	40.99	(Osayi et al., 2018)
FxB	FxB	WCT	9	20	550	30	35.69	52.61	11.7	(Boxiong et al., 2007)
FxB	FxB	WT	0.42	50	550	15	33	38	29	(Díez et al., 2005)
FxB	FxB	WMT	1.75	130	550	1	42	47.7	7.4	(Ucar et al., 2005)
FxB	FxB	TT		130	550	1	33.8	55.6	7.6	(Ucar et al., 2005)
FxB	FxB		110		550		33	56	10	(Roy et al., 1999)
FxB	FxB	WT	0.35	100	550		36.9	47.1	16	(Zhang et al., 2008)
FxB	FxB	WT	13	15	570	100	40.7	50	9.3	(Bajus and Olahová, 2011)
FxB	FxB	WMT	15		575	50	41	42	18	(Islam et al., 2008)
FxB	FxB	WCT	9	20	600	30	36.3	54.1	9.61	(Boxiong et al., 2007)
FxB	FxB	WT	1.5		600	120	36.58	30.89	28.74	(Choi et al., 2014)
FxB	FxB	WCT		175	600	30	44.2	38.2	17.5	(de Marco Rodriguez et al., 2001)
FxB	FxB	WT	0.35	100	600		34.8	48.8	16.3	(Zhang et al., 2008)
FxB	FxB	WT	2	10	600		37.79	18.88	43.33	(Osayi et al., 2018)
FxB	FxB	WT	2	10	600		34.36	22.89	42.75	(Osayi et al., 2018)
FxB	FxB	WT	2	10	600		33	24.5	42.5	(Osayi et al., 2018)
FxB	FxB	WMT	1.75	130	650	1	41.7	48.4	7.6	(Ucar et al., 2005)
FxB	FxB	TT		130	650	1	33.8	56	7.6	(Ucar et al., 2005)
FxB	FxB	LiWT	20	0.2	650		40	51	9.1	(Singh et al., 2018)
MeB	RK	WT	7.5		450		34.77	50.74	7.54	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	7.5		450		32.14	51.28	10.32	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		450		34.55	50.91	10.08	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		450		32.48	51.33	10.1	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	17.5		450		32.03	51	3.32	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	17.5		450		33.05	51.61	10.95	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	7.5		500		35.12	49.98	10.75	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	7.5		500		33.92	50.14	11.04	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		500		34.99	49.13	10.86	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		500		33.72	51.56	9.26	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	17.5		500		34.98	49.92	9.17	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	17.5		500		33.66	51.78	7.92	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	7.5		550		34.84	48.28	12.55	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	7.5		550		34.14	50.02	8.45	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		550		34.83	47.59	11.08	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		550		34.59	51.47	7.09	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	17.5		550		35.6	47.06	12.71	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	17.5		550		35.5	51.83	12.11	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	7.5		600		34.9	46.13	10.7	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	7.5		600		34.32	49.85	11.77	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		600		33.69	47	10.8	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	12.5		600		33.72	50.32	10.61	(Antoniou and Zabaniotou, 2015)
MeB	RK	WT	17.5		600		33.57	47.13	13.66	(Antoniou and Zabaniotou, 2015)

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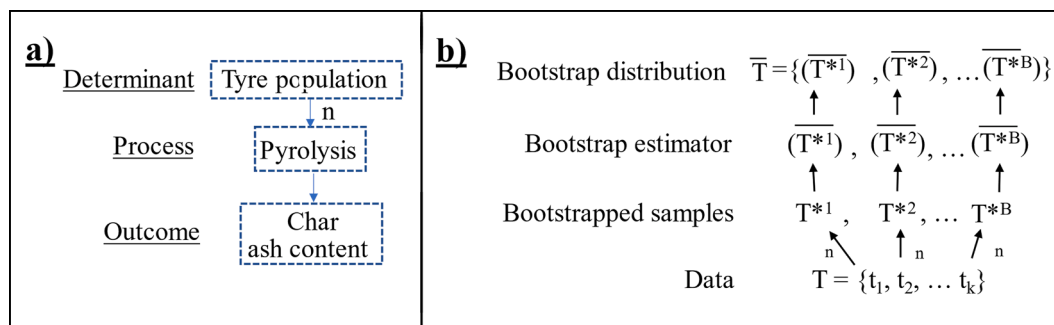
RT	RST	FS	PS (mm)	SM (g)	HHT (°C)	Ti (min)	Char (%)	Oil (%)	Gas (%)	Ref
MeB	RK	WT	17.5		600		32.92	51.14	7.31	(Antoniou and Zabaniotou, 2015)
MeB	ABR	WT	1.3		495	21.5	34.4	54.2	11.5	(Black and Brown, 1992)
MeB	ABR	WT	3.4		570	11.8	34.8	49.8	15.4	(Black and Brown, 1992)
MeB	A/S		1.5	400	497	4	38.3	51.2	7.5	(Choi et al., 2016)
MeB	A/S		1.5	400	516	4	36.8	49.1	11.2	(Choi et al., 2016)
MeB	A/S		1.5	400	614	4	36.5	41	19	(Choi et al., 2016)
MeB	A/S		1.5	400	617	4	37.3	39	20.4	(Choi et al., 2016)
MeB	A/S	WT	2		500	450	45.6	39.9	14.5	(Frigo et al., 2014)
MeB	A/S	WT	2		500	450	47	43.2	9.8	(Frigo et al., 2014)
MeB	A/S	WT	2		500	450	50	45	5	(Frigo et al., 2014)
MeB	A/S	WT	2		500	450	53.3	42.2	4.5	(Frigo et al., 2014)
MeB	RK	WT	14	50,000	450		43.9	43.9	13.1	(Li et al., 2004)
MeB	RK	WT	14	50,000	500		41.3	45.1	13.6	(Li et al., 2004)
MeB	RK	WT	14	50,000	550		39.9	44.6	15.5	(Li et al., 2004)
MeB	RK	WT	14	50,000	600		39.3	42.7	18	(Li et al., 2004)
MeB	RK	WT	14	50,000	650		38.8	42.9	18.3	(Li et al., 2004)
MeB	BM	WT	0.35		500	30	40	55.5	4.5	(W. Li et al., 2016)
MeB	A/S	WT			500		37	55	7.5	(Lozhechnik and Savchin, 2016)
MeB	A/S	WT	3	40,000	550	3	40.7	42.4	17	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	39.2	42.7	18.1	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	39.2	43.3	17.4	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	39.7	42.7	17.7	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	39.2	43.1	17.8	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	39.4	42.9	17.7	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	40	42	18	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	42.3	41.8	15.9	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	42.3	42.6	15.1	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	42.2	42.3	15.5	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	41.4	41.9	16.7	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	41.3	42.4	16.4	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	40.1	43.6	16.3	(Martínez et al., 2019)
MeB	A/S	WT	3	40,000	550	3	40.5	42.6	16.9	(Martínez et al., 2019)
MeB	RK		14	546,000	534		30.3	53.7	7	(Pakdel et al., 2001)
MeB	ABR				550		33.5	49.6	16.9	(Peacocke and Bridgwater, 1993)
MeB	RK	TT	110	180,000	485		39	43	5	(Roy et al., 1999)
MeB	RK	WCT	500	180,000	500		37	47	5	(Roy et al., 1999)
MeB	RK	WCT	110	80,000	520		36	45	6	(Roy et al., 1999)
MeB	RK	WCT	25	158,000	550		33	56	10	(Roy et al., 1999)
FIB	CFIB	WT	0.8		450		28.5	52	15	(Dai et al., 2001)
FIB	BB		0.3		475		45.5	36.12	18.38	(Raj et al., 2013)
FIB	BB		0.72		475		24.5	41.5	34	(Raj et al., 2013)
FIB	BB		0.71		475		34.5	40.6	24.9	(Raj et al., 2013)
FIB	BB		0.71		475		24.5	41.5	34	(Raj et al., 2013)
FIB	BB		0.71		475		24.5	41.5	34	(Raj et al., 2013)
FIB	BB		0.71		475		34.5	40.6	24.9	(Raj et al., 2013)
FIB	BB		0.71		475		24.5	41.5	34	(Raj et al., 2013)
FIB	BB		0.71		475		26	40	34	(Raj et al., 2013)
FIB	BB		0.71		475		29.85	42.4	27.75	(Raj et al., 2013)
FIB	BB		1.18		475		30.25	39.25	30.5	(Raj et al., 2013)
FIB	SpB	WTT	3	65	475	50	35.9	58.2	5.9	(Alvarez et al., 2017)
FIB	SpB	WTT	0.55		475	30	35.9	58.22	5.91	(Lopez et al., 2017)
FIB	BB	WT	1.5		497	80	38.3	51.2	7.5	(Choi et al., 2016)
FIB	SpB	UR	13	2	500		33.7	63.4	2.7	(Arabiourrutia et al., 2007)
FIB	BB	UR	1.5	2926	500	143	31	65	3.5	(Kaminsky and Mennerich, 2001)
FIB	BB	UR	1	3960	500	230	30	65	5	(Kaminsky and Mennerich, 2001)
FIB	SpB	UR	1		500		34	55.3	3	(Arabiourrutia et al., 2007)
FIB	SpB	ULR	1	100	500		36.92	60.89	2.18	(Kaminsky and Mennerich, 2001)
FIB	SpB	UCR	1	100	500		34.05	61.7	4.25	(Kaminsky and Mennerich, 2001)
FIB	SpB	WT	1		500		34.4	62.4	4.3	(Lopez et al., 2010)
FIB	SpB	WT	1	100	500		34.5	62.2	4.1	(Lopez et al., 2010)
FIB	SpB	WT	1	100	500		34.2	60.5	5.9	(Lopez et al., 2010)
FIB	CfIB	WT	0.32		500		31.6	50.5	14.5	(Dai et al., 2001)
FIB	CfIB	WT	0.8		500		45.4	41.3	10	(Dai et al., 2001)
FIB	CfIB	WT	0.32		500	1s	14.5	50	31.5	(Dai et al., 2001)
FIB	CfIB	WT	0.32		500	3s	17.5	48.7	29.5	(Dai et al., 2001)
FIB	CfIB	WT	0.32		500	5s	21.5	46.3	28.2	(Dai et al., 2001)
FIB	BB	WT	1.5		516	80	36.8	49.1	11.2	(Choi et al., 2016)
FIB	SpB	UR	13	2	550		33.7	63.3	2.3	(Arabiourrutia et al., 2007)
FIB	BB	UR	1.5	3969	550	220	34	57	9.2	(Kaminsky and Mennerich, 2001)
FIB	BB		0.48		550		40.54	29.3	30.16	(Raj et al., 2013)
FIB	BB		0.48		550		26.25	28.25	45.5	(Raj et al., 2013)
FIB	BB		1		550		30.45	32	37.58	(Raj et al., 2013)
FIB	BB		1		550		30.8	35.2	34	(Raj et al., 2013)
FIB	SpB	UR	1		550		34	50	3	(Arabiourrutia et al., 2007)
FIB	SpB	WTT	3	65	575	50	35.9	54	10.1	(Alvarez et al., 2017)
FIB	SpB	WTT	0.55		575	30	35.9	53.96	10.16	(Lopez et al., 2017)

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RT	RST	FS	PS (mm)	SM (g)	HHT (°C)	Ti (min)	Char (%)	Oil (%)	Gas (%)	Ref
FIB	BB		1.3	5120	598	215	27.5	45.9	18.3	(Kaminsky et al., 2009)
FIB	BB		1.3	5000	599	175	30.3	45.8	17.5	(Kaminsky et al., 2009)
FIB	BB	UR	1.5	3587	600	240	40	51	9.1	(Kaminsky et al., 2009)
FIB	BB		1.3	6000	600	190	28.6	46	19.3	(Kaminsky et al., 2009)
FIB	BB		0.71		600		28.7	25.3	46	(Raj et al., 2013)
FIB	SpB	ULR	1	100	600		38.3	54.95	6.81	(Lopez et al., 2009)
FIB	SpB	UCR	1	100	600		35.81	55.94	8.26	(Lopez et al., 2009)
FIB	CFIB	WT	0.32		600		28	48.5	20	(Dai et al., 2001)
FIB	BB		1.3	5949	601	180	29.4	46.8	15.5	(Kaminsky et al., 2009)
FIB	SpB	UR	13	2	610		34.3	32.3	3	(Arabiourrutia et al., 2007)
FIB	SpB	UR	1		610		34	62.8	3	(Arabiourrutia et al., 2007)
FIB	BB	WT	1.5		614	80	26.5	41	19	(Choi et al., 2016)
FIB	BB	WT	1.5		617	80	37.3	39	20.4	(Choi et al., 2016)
FIB	BB		1.3	31,000	650	140	27.6	46.4	22.1	(Kaminsky et al., 2009)
FIB	BB		500		650		35	25	17.5	(Kaminsky, 1993)

Appendix C. Graphical and statistical representations of the bootstrapping method



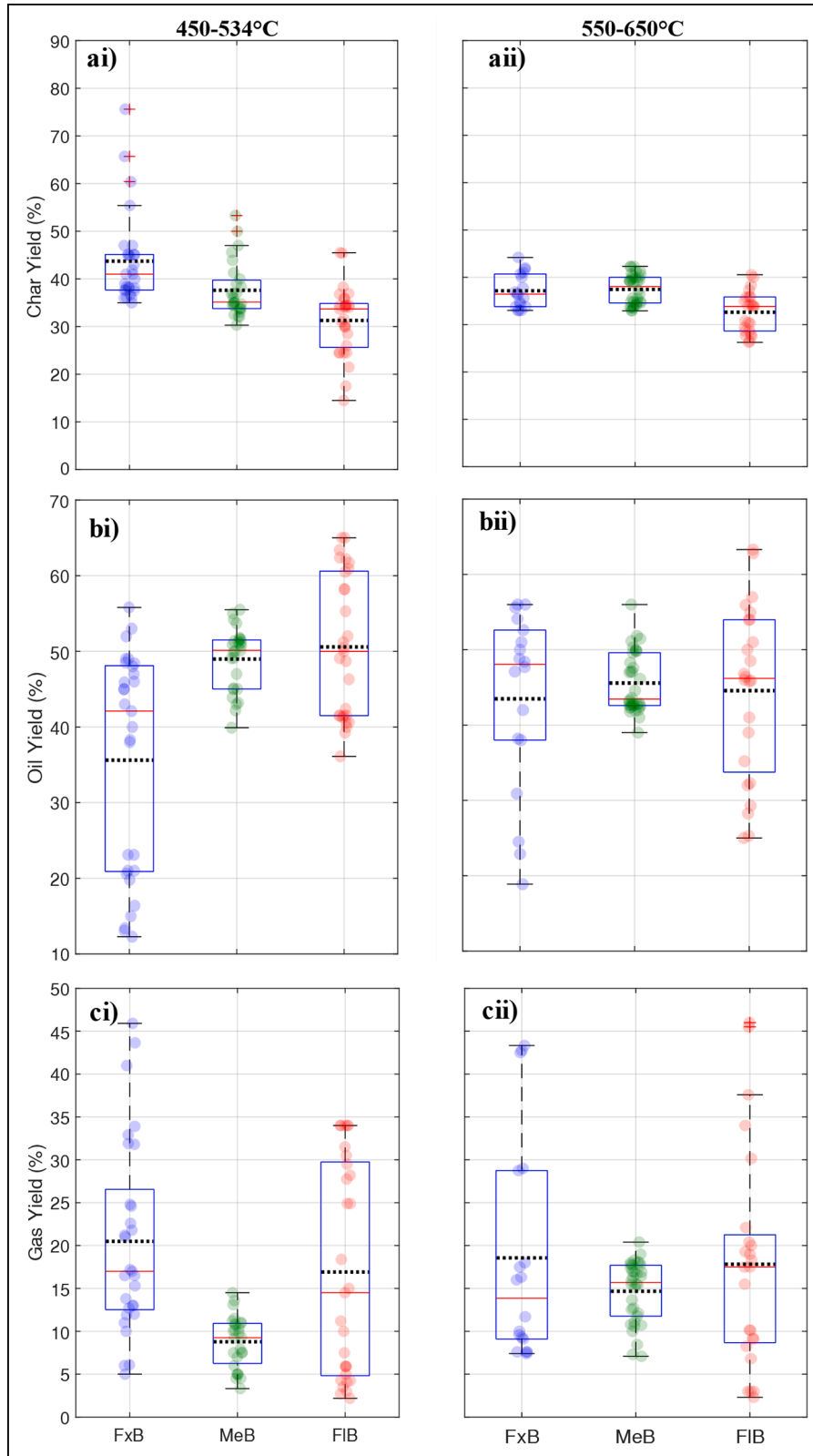
Appendix D. Maximum likelihood estimator (average) and spread of tyre feedstock data (Appendix A). Average is displayed as the median. Range is displayed as the interquartile range between the 2.5–97.5% quantiles, i.e. the average 95% of tyres analysed

		FC	Ash	VM	M	C	H	N	S	(P-Char-Y) _{CC}	P-Char-Ash _{CC}
Range (95%)	Average (%)	28.09	4.7	64.9	0.8	84.3	7	0.494	1.88	34.3	16.48
	Low (%)	19.4	2.16	56.4	0.24	74.27	5.57	0.22	0.32	23.6	6.58
	High (%)	32.25	19.9	76.1	1.79	89.5	8.77	3.29	3.05	43.0	48.9

Appendix E. Median and range of values of pyrolysis product yields (Appendix B) for char, oil and gas. Range reported as a 95% confidence interval, from 2.5% (QL) to 97.5% (QH) quantiles

	Char			Oil			Gas			n
	Av	QL	QH	Av	QL	QH	Av	QL	QH	
All runs	35.9	24.5	54.3	46.8	15.7	63.0	13.6	3.0	43.5	161
Fixed beds	38.4	33.0	68.9	45.0	12.8	56.0	16.5	5.7	44.4	47
450–534 °C	41.0	35.2	73.4	42.0	12.5	55.2	17.0	5.2	45.4	29
535–650 °C	36.4	33.0	44.2	48.0	18.9	56.0	13.9	7.4	43.3	18
Mechanically mixed beds	36.5	32.0	49.9	47.1	39.9	55.5	11.2	4.5	19.0	61
450–534 °C	35.1	30.6	52.7	50.1	40.3	55.4	9.3	3.5	14.3	27
535–650 °C	38.1	32.9	42.3	43.5	39.7	54.5	15.7	7.2	19.9	34
Fluidised beds	33.7	17.0	45.4	48.5	25.2	65.0	15.5	2.3	45.6	53
450–534 °C	33.7	15.2	45.5	50.0	36.8	65.0	14.5	2.3	34.0	29
535–650 °C	33.85	26.3	40.5	46.2	25.0	63.3	17.5	2.4	46.0	24

Appendix F. Box plots of yields: a) char, b) oil and c) gas as a function of reactor type (Fixed bed: FxB, blue; Mechanically mixed bed: MeB, green; Fluidised bed: FIB, red) and HHT: i) low (450–534 °C) and ii) high (535–650 °C). Boxes, whiskers, solid and dotted horizontal lines represent interquartile range, non-outliers (See MATLAB ‘boxplot’ documentation for details on outlier specification, $w = 1.5$), outliers, median and mean values, respectively. Points outside of the whiskers are considered outliers



References

- Aguado, R., Olazar, M., Vélez, D., Arabiourrutia, M., Bilbao, J., 2005. Kinetics of scrap tyre pyrolysis under fast heating conditions. *J. Anal. Appl. Pyrolysis* 73, 290–298. <https://doi.org/10.1016/j.jaap.2005.02.006>.
- Aguado, J., Serrano, D.P., Escola, J.M., 2006. Catalytic upgrading of plastic wastes. *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels* 73–110. <https://doi.org/10.1002/0470021543.ch3>.
- Ahmed, M.B., et al., 2019. Activated carbon preparation from biomass feedstock: clean production and carbon dioxide adsorption. *J. Clean. Prod.* 225, 405–413. <https://doi.org/10.1016/j.jclepro.2019.03.342>.
- Ahoor, A.H., Zandi-Atashbar, N., 2014. Fuel production based on catalytic pyrolysis of waste tires as an optimized model. *Energy Convers. Manage.* 87, 653–669. <https://doi.org/10.1016/j.enconman.2014.07.033>.
- Akkouche, N., et al., 2017. Heating rate effects on pyrolytic vapors from scrap truck tires. *J. Anal. Appl. Pyrolysis* 123, 419–429. <https://doi.org/10.1016/j.jaap.2016.10.005>.
- Al-Rahbi, A.S., Williams, P.T., 2017. Hydrogen-rich syngas production and tar removal from biomass gasification using sacrificial tyre pyrolysis char. *Appl. Energy* 190, 501–509. <https://doi.org/10.1016/j.apenergy.2016.12.099>.
- Al-Salem, S.M., Lettieri, P., Baeyens, J., 2009. Kinetics and product distribution of end of life tyres (ELTs) pyrolysis: a novel approach in polyisoprene and SBR thermal cracking. *J. Hazard. Mater.* 172 (2–3), 1690–1694. <https://doi.org/10.1016/j.jhazmat.2009.07.127>.
- Alvarez, J., Amutio, M., Lopez, G., Santamaria, L., Bilbao, J., Olazar, M., 2019. Improving bio-oil properties through the fast co-pyrolysis of lignocellulosic biomass and waste tyres. *Waste Manag.* 85, 385–395. <https://doi.org/10.1016/j.wasman.2019.01.003>.
- Alvarez, J., Lopez, G., Amutio, M., Mkhize, N.M., Danon, B., van der Gryp, P., et al., 2017a. Evaluation of the properties of tyre pyrolysis oils obtained in a conical spouted bed reactor. *Energy* 128, 463–474.
- Amari, T., Themelis, N.J., Wernick, I.K., 1999. Resource recovery from used rubber tires. *Resour. Policy* 25 (3), 179–188. [https://doi.org/10.1016/S0301-4207\(99\)00025-2](https://doi.org/10.1016/S0301-4207(99)00025-2).
- Amri, N., Zakaria, R., Bakar, M.Z., 2009. Adsorption of phenol using activated carbon adsorbent from waste tyres. *Pertanika J. Sci. Technol.* 17 (2), 371–380.
- Anjum, A., et al., 2019. Role of recovered carbon black ash content composition on in-rubber performance. In: *International Rubber Conference, IRC 2019*.
- Antoniou, N., Stavropoulos, G., Zabaniotou, A., 2014. Activation of end of life tyres pyrolytic char for enhancing viability of pyrolysis—Critical review, analysis and recommendations for a hybrid dual system. *Renew. Sustain. Energy Rev.* 39, 1053–1073. <https://doi.org/10.1016/j.rser.2014.07.143>.
- Antoniou, N., Zabaniotou, A., 2015. Experimental proof of concept for a sustainable End of Life Tyres pyrolysis with energy and porous materials production. *J. Clean. Prod.* 101, 323–336. <https://doi.org/10.1016/j.jclepro.2015.03.101>.
- Arabiourrutia, M., et al., 2007. Product distribution obtained in the pyrolysis of tyres in a conical spouted bed reactor. *Chem. Eng. Sci.* 62 (18–20), 5271–5275. <https://doi.org/10.1016/j.ces.2006.12.026>.
- Arabiourrutia, M., et al., 2019. Coupling gas flow pattern and kinetics for tyre pyrolysis modelling. *Chem. Eng. Sci.* 201, 362–372. <https://doi.org/10.1016/j.ces.2019.02.025>.
- Arabiourrutia, M., et al., 2020. Waste tyre valorization by catalytic pyrolysis—A review. *Renew. Sustain. Energy Rev.* 129, 109932. <https://doi.org/10.1016/j.rser.2020.109932>.
- Arya, Saksham, Sharma, Abhishek, Rawat, Manish, Agrawal, Alok, 2020. Tyre pyrolysis oil as an alternative fuel: A review. *Materials Today: Proceedings* 28, 2481–2484. <https://doi.org/10.1016/j.matpr.2020.04.797>.
- Aslan, D.I., Parthasarathy, P., Goldfarb, J.L., Ceylan, S., 2017. Pyrolysis reaction models of waste tires: Application of Master-Plots method for energy conversion via devolatilization. *Waste Manag.* 68, 405–411. <https://doi.org/10.1016/j.wasman.2017.06.006>.
- Athanassiades, E., 2013. *Waste tyre pyrolysis: Sustainable recovery and reuse of a valuable resource*. Imperial College, London.
- Aylón, E., et al., 2005. Assessment of tyre devolatilization kinetics. *J. Anal. Appl. Pyrolysis* 74 (1–2), 259–264. <https://doi.org/10.1016/j.jaap.2004.09.006>.
- Aylón, E., et al., 2010. Valorisation of waste tyre by pyrolysis in a moving bed reactor. *Waste Manage. (Oxford)* 30 (7), 1220–1224. <https://doi.org/10.1016/j.wasman.2009.10.001>.
- Aziz, M.A., et al., 2017. Design and fabrication of a fixed-bed batch type pyrolysis reactor for pilot scale pyrolytic oil production in Bangladesh. In: *IOP Conference Series: Materials Science and Engineering*. <https://doi.org/10.1088/1757-899X/184/1/012056>.
- Bajus, M., Olahová, N., 2011. Thermal conversion of scrap tyres. *Petroleum & Coal* 53 (2).
- Banar, M., et al., 2015. Evaluation of solid product obtained from tire-derived fuel (TDF) pyrolysis as carbon black. *J. Mater. Cycles Waste Manage.* 17 (1), 125–134. <https://doi.org/10.1007/s10163-014-0233-2>.
- Bernardo, M., et al., 2012. Study of the organic extraction and acidic leaching of chars obtained in the pyrolysis of plastics, tire rubber and forestry biomass wastes. *Procedia Eng.* 42, 1739–1746. <https://doi.org/10.1016/j.proeng.2012.07.567>.
- Black, J. and Brown, D. (1992) *Development of a continuous ablative reactor for fast pyrolysis*.
- Boxiong, S., Chunfei, W., Cai, L., et al., 2007a. Pyrolysis of waste tyres: the influence of USY catalyst/tyre ratio on products. *J. Anal. Appl. Pyrolysis* 78 (2), 243–249.
- Butler, E., et al., 2011. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renew. Sustain. Energy Rev.* 15 (8), 4171–4186. <https://doi.org/10.1016/j.rser.2011.07.035>.
- Campuzano, F., Abdul Jameel, A.G., Zhang, W., Emwas, A.-H., Agudelo, A.F., Martínez, J.D., Sarathy, S.M., 2020. Fuel and chemical properties of waste tyre pyrolysis oil derived from a continuous twin-auger reactor. *Energy & Fuels* 34, 12688–12702. <https://doi.org/10.1021/acs.energyfuels.0c02271>.
- Cardona, N., Campuzano, F., Betancur, M., Jaramillo, L., Martínez, J.D., 2018. Possibilities of carbon black recovery from waste tyre pyrolysis to be used as additive in rubber goods—a review. *IOP Publishing, p. 12012*. <https://doi.org/10.1088/1757-899X/437/1/012012>.
- Cataldo, F., 2020. On the characterisation of carbon black from tyre pyrolysis. *Fullerenes, Nanotubes and Carbon Nanostructures* 28 (5), 368–376. <https://doi.org/10.1080/1536383X.2019.1685983>.
- Chaalaa, A., Roy, C., Ait-Kadi, A., 1996. Rheological properties of bitumen modified with pyrolytic carbon black. *Fuel* 75 (13), 1575–1583. [https://doi.org/10.1016/0016-2361\(96\)00143-3](https://doi.org/10.1016/0016-2361(96)00143-3).
- Chan, O.S., Cheung, W.H., McKay, G., 2011. Preparation and characterisation of demineralised tyre derived activated carbon. *Carbon N Y* 49 (14), 4674–4687. <https://doi.org/10.1016/j.carbon.2011.06.065>.
- Chang, B.P., et al., 2021. Bioresourced fillers for rubber composite sustainability: current development and future opportunities. *Green Chem.* 23 (15), 5337–5378. <https://doi.org/10.1039/D1GC01115D>.
- Cheah, S., Malone, S.C., Feik, C.J., 2014. Speciation of sulfur in biochar produced from pyrolysis and gasification of oak and corn stover. *Environ. Sci. Technol.* 48 (15), 8474–8480. <https://doi.org/10.1021/es500073r>.
- Cheung, K.-Y., et al., 2011. Integrated kinetics and heat flow modelling to optimise waste tyre pyrolysis at different heating rates. *Fuel Process. Technol.* 92 (5), 856–863. <https://doi.org/10.1016/j.fuproc.2010.11.028>.
- Chinyama, M.P.M. (2011) “Alternative fuels in cement manufacturing,” in *Alternative fuel*. IntechOpen.
- Choi, G.-G., et al., 2014. Total utilization of waste tyre rubber through pyrolysis to obtain oils and CO₂ activation of pyrolysis char. *Fuel Process. Technol.* 123, 57–64. <https://doi.org/10.1016/j.fuproc.2014.02.007>.
- Choi, G.-G., Oh, S.-J., Kim, J.-S., 2016. Non-catalytic pyrolysis of scrap tyres using a newly developed two-stage pyrolyzer for the production of a pyrolysis oil with a low sulfur content. *Appl. Energy* 170, 140–147. <https://doi.org/10.1016/j.apenergy.2016.02.119>.
- Clark, C., Meardon, K., Russell, D., 1993. *Scrap Tire Technology and Markets*. William Andrew Inc.
- Conesa, J.A., et al., 2008. Organic and inorganic pollutants from cement kiln stack feeding alternative fuels. *J. Hazard. Mater.* 158 (2–3), 585–592. <https://doi.org/10.1016/j.jhazmat.2008.01.116>.
- Cunliffe, A.M., Williams, P.T., 1998a. Composition of oils derived from the batch pyrolysis of tyres. *J. Anal. Appl. Pyrolysis* 44 (2), 131–152.
- Dai, X., et al., 2001. Pyrolysis of waste tires in a circulating fluidized-bed reactor. *Energy* 26 (4), 385–399. [https://doi.org/10.1016/S0360-5442\(01\)00003-2](https://doi.org/10.1016/S0360-5442(01)00003-2).
- Dick, D.T., Agboola, O., Ayeni, A.O., 2020. Pyrolysis of waste tyre for high-quality fuel products: a review [J]. *AIMS Energy* 8 (5), 869–895.
- Díez, C., et al., 2005. Pyrolysis of tyres: a comparison of the results from a fixed-bed laboratory reactor and a pilot plant (rotary reactor). *J. Anal. Appl. Pyrolysis* 74 (1–2), 254–258. <https://doi.org/10.1016/j.jaap.2004.11.024>.
- Doja, S., Pillari, L.K., Bichler, L., 2022. Processing and activation of tyre-derived char: A review. *Renew. Sustain. Energy Rev.* 155, 111860. <https://doi.org/10.1016/j.rser.2021.111860>.
- Düng, N.A., et al., 2009. Light olefins and light oil production from catalytic pyrolysis of waste tyre. *J. Anal. Appl. Pyrolysis* 86 (2), 281–286. <https://doi.org/10.1016/j.jaap.2009.07.006>.
- EC, 1999. Council directive 1999/31/EC of 26 April 1999 on the landfill of waste. *Official Journal of the European Communities L* 269, 19.
- Efron, B., Tibshirani, R.J., 1994. *An introduction to the bootstrap*. CRC press.
- Elbaba, I.F., Williams, P.T., 2012. Two stage pyrolysis-catalytic gasification of waste tyres: influence of process parameters. *Appl. Catal. B* 125, 136–143. <https://doi.org/10.1016/j.apcatb.2012.05.020>.
- Elbaba, I.F., Wu, C., Williams, P.T., 2011. Hydrogen production from the pyrolysis-gasification of waste tyres with a nickel/cerium catalyst. *Int. J. Hydrogen Energy* 36 (11), 6628–6637. <https://doi.org/10.1016/j.ijhydene.2011.02.135>.
- Evans, A., Evans, R., 2006. The composition of a tyre: typical components. *The Waste & Resources Action Programme* 5.
- Fan, Y., Fowler, G.D., 2018. The potential of pyrolytic biomass as a sustainable biofiller for styrene-butadiene rubber. *Adv. Surf. Eng. Res.* <https://doi.org/10.5772/INTECHOPEN.79994> [Preprint].
- Fan, Y., Fowler, G.D., Zhao, M., 2020a. The past, present and future of carbon black as a rubber reinforcing filler—A review. *J. Clean. Prod.* 247, 119115.
- Fleck, T., 2021. Fraunhofer process recovers carbon black from waste tyres. *Adit. Polym.* (7), 5–6. [https://doi.org/10.1016/S0306-3747\(21\)00128-7](https://doi.org/10.1016/S0306-3747(21)00128-7), 2021.
- Forrest, M., 2014. *Recycling and Re-Use of Waste Rubber*. Smithers Rapra.
- Frijo, S., et al., 2014. Liquid fuel production from waste tyre pyrolysis and its utilisation in a Diesel engine. *Fuel* 116, 399–408. <https://doi.org/10.1016/j.fuel.2013.08.044>.
- Galvagno, S., et al., 2002. Pyrolysis process for the treatment of scrap tyres: preliminary experimental results. *Waste Manage. (Oxford)* 22 (8), 917–923. [https://doi.org/10.1016/S0956-053X\(02\)00083-1](https://doi.org/10.1016/S0956-053X(02)00083-1).
- Gamboa, A.R., et al., 2020. Tyre pyrolysis oil in Brazil: potential production and quality of fuel. *Renew. Sustain. Energy Rev.* 120, 109614. <https://doi.org/10.1016/j.rser.2019.109614>.
- García-Freites, S., Gough, C., Röder, M., 2021. The greenhouse gas removal potential of bioenergy with carbon capture and storage (BECCS) to support the UK’s net-zero emission target. *Biomass Bioenergy* 151, 106164. <https://doi.org/10.1016/j.biombioe.2021.106164>.

- Ghose, S., Isayev, A.I., 2003. Recycling of unfilled polyurethane rubber using high-power ultrasound. *J. Appl. Polym. Sci.* 88 (4), 980–989. <https://doi.org/10.1002/app.11740>.
- Groves, S.A., et al., 1991. Natural rubber pyrolysis: study of temperature-and thickness-dependence indicates dimer formation mechanism. *J. Anal. Appl. Pyrolysis* 19, 301–309. [https://doi.org/10.1016/0165-2370\(91\)80051-9](https://doi.org/10.1016/0165-2370(91)80051-9).
- Heralan, A., 1978. On the formation of polycyclic aromatics: investigation of fuel oil and emissions by high-resolution mass spectrometry. *Combust. Flame* 31, 297–307. [https://doi.org/10.1016/0010-2180\(78\)90142-6](https://doi.org/10.1016/0010-2180(78)90142-6).
- Hoyer, S., Kroll, L., Sykuter, D., 2020. Technology comparison for the production of fine rubber powder from end of life tyres. *Procedia Manuf.* 43, 193–200. <https://doi.org/10.1016/j.promfg.2020.02.135>.
- I.E.A., 2008. CO2 Emissions from Fuel Combustion: 1972. International Energy Agency.
- Islam, M.R., et al., 2011. Feasibility study for thermal treatment of solid tire wastes in Bangladesh by using pyrolysis technology. *Waste Manage. (Oxford)* 31 (9–10), 2142–2149. <https://doi.org/10.1016/j.wasman.2011.04.017>.
- Islam, M.R., Haniu, H., Beg, M.R.A., 2008a. Liquid fuels and chemicals from pyrolysis of motorcycle tire waste: product yields, compositions and related properties. *Fuel* 87 (13–14), 3112–3122.
- Januszewicz, K., et al., 2020. Waste tyres pyrolysis for obtaining limonene. *Materials (Basel)* 13 (6), 1359. <https://doi.org/10.3390/ma13061359>.
- Jimoda, L.A., et al., 2018. Assessment of environmental impact of open burning of scrap tyres on ambient air quality. *Int. J. Environ. Sci. Technol.* 15 (6), 1323–1330. <https://doi.org/10.1007/s13762-017-1498-5>.
- Jones, I., Zhu, M., Zhang, J., Zhang, Z., Preciado-Hernandez, J., Gao, J., Zhang, D., 2021. The application of spent tyre activated carbons as low-cost environmental pollution adsorbents: A technical review. *J. Clean. Prod.* 312, 127566. <https://doi.org/10.1016/j.jclepro.2021.127566>.
- Kaminsky, W., 1993a. Recycling of polymers by pyrolysis. *Le Journal de Physique IV* 3 (C7), C7–1543.
- Kaminsky, W., Mennerich, C., 2001. Pyrolysis of synthetic tire rubber in a fluidised-bed reactor to yield 1, 3-butadiene, styrene and carbon black. *J. Anal. Appl. Pyrolysis* 58, 803–811. [https://doi.org/10.1016/S0165-2370\(00\)00129-7](https://doi.org/10.1016/S0165-2370(00)00129-7).
- Kaminsky, W., Mennerich, C., Zhang, Z., 2009. Feedstock recycling of synthetic and natural rubber by pyrolysis in a fluidized bed. *J. Anal. Appl. Pyrolysis* 85 (1–2), 334–337. <https://doi.org/10.1016/j.jaap.2008.11.012>.
- Kaminsky, W., Sinn, H., 1980. Pyrolysis of plastic waste and scrap tires using a fluidized-bed process. ACS Publications. <https://doi.org/10.1021/bk-1980-0130.ch031>.
- Kar, Y., 2011. Catalytic pyrolysis of car tire waste using expanded perlite. *Waste Manage. (Oxford)* 31 (8), 1772–1782. <https://doi.org/10.1016/j.wasman.2011.04.005>.
- Karatas, H., et al., 2013. Experimental results of gasification of waste tire with air in a bubbling fluidized bed gasifier. *Fuel* 105, 566–571. <https://doi.org/10.1016/j.fuel.2012.08.038>.
- Khan, S.R., et al., 2021. A comprehensive study on upgradation of pyrolysis products through co-feeding of waste tire into rice straw under broad range of co-feed ratios in a bench-scale fixed bed reactor. *Biomass Convers. Biorefin.* 2021, 1–15. <https://doi.org/10.1007/S13399-021-01434-9>.
- Koury, J., 2018. Committee D36 on recovered carbon black (rCB). *Astm.Org [Preprint]*.
- Kumaravel, S.T., Murugesan, A., Kumaravel, A., 2016. Tyre pyrolysis oil as an alternative fuel for diesel engines—A review. *Renew. Sustain. Energy Rev.* 60, 1678–1685. <https://doi.org/10.1016/j.rser.2016.03.035>.
- Kuśmierk, K., Świątkowski, A., Kotkowski, T., Cherbański, R., Molga, E., 2021. Adsorption on activated carbons from end-of-life tyre pyrolysis for environmental applications. Part I. preparation of adsorbent and adsorption from gas phase. *J. Anal. Appl. Pyrolysis* 157, 105205. <https://doi.org/10.1016/j.jaap.2021.105205>.
- Kuśmierk, K., Świątkowski, A., Kotkowski, T., Cherbański, R., Molga, E., 2021. Adsorption on activated carbons from end-of-life tyre pyrolysis for environmental applications. Part II. Adsorption from aqueous phase. *J. Anal. Appl. Pyrolysis* 158, 105206. <https://doi.org/10.1016/j.jaap.2021.105206>.
- Kwon, E., Castaldi, M.J., 2009. Fundamental understanding of the thermal degradation mechanisms of waste tires and their air pollutant generation in a N2 atmosphere. *Environ. Sci. Technol.* 43 (15), 5996–6002. <https://doi.org/10.1021/es900564b>.
- Lay, M., et al., 2020. Converting dead leaf biomass into activated carbon as a potential replacement for carbon black filler in rubber composites. *Compos. B. Eng.* 201, 108366. <https://doi.org/10.1016/J.COMPOSITESB.2020.108366>.
- Leung, D.Y.C., Wang, C.L., 1998. Kinetic study of scrap tyre pyrolysis and combustion. *J. Anal. Appl. Pyrolysis* 45 (2), 153–169. [https://doi.org/10.1016/S0165-2370\(98\)00065-5](https://doi.org/10.1016/S0165-2370(98)00065-5).
- Lewandowski, W.M., Januszewicz, K., Kosakowski, W., 2019. Efficiency and proportions of waste tyre pyrolysis products depending on the reactor type—A review. *J. Anal. Appl. Pyrolysis* 140, 25–53. <https://doi.org/10.1016/j.jaap.2019.03.018>.
- Li, S.-Q., et al., 2004. Pilot-scale pyrolysis of scrap tires in a continuous rotary kiln reactor. *Ind. Eng. Chem. Res.* 43 (17), 5133–5145. <https://doi.org/10.1021/ie030115m>.
- Li, W., et al., 2016a. Derived oil production by catalytic pyrolysis of scrap tires. *Chin. J. Catal.* 37 (4), 526–532. [https://doi.org/10.1016/S1872-2067\(15\)60998-6](https://doi.org/10.1016/S1872-2067(15)60998-6).
- Lopez, G., et al., 2009. Influence of tire formulation on the products of continuous pyrolysis in a conical spouted bed reactor. *Energy Fuels* 23 (11), 5423–5431. <https://doi.org/10.1021/ef900582k>.
- López, G., et al., 2010. Continuous pyrolysis of waste tyres in a conical spouted bed reactor. *Fuel* 89 (8), 1946–1952. <https://doi.org/10.1016/j.fuel.2010.03.029>.
- Lopez, G., et al., 2010. Vacuum pyrolysis of waste tires by continuously feeding into a conical spouted bed reactor. *Ind. Eng. Chem. Res.* 49 (19), 8990–8997. <https://doi.org/10.1021/ie1000604>.
- Lopez, G., Alvarez, J., Amutio, M., Mkhize, N.M., Danon, B., van der Gryp, P., et al., 2017a. Waste truck-tyre processing by flash pyrolysis in a conical spouted bed reactor. *Energy Convers. Manage.* 142, 523–532.
- Lozhechnik, A.V., Savchin, V.V., 2016. Pyrolysis of rubber in a screw reactor. *J. Eng. Phys. Thermophys.* 89 (6), 1482–1486. <https://doi.org/10.1007/s10891-016-1517-2>.
- Malkov, T., 2004. Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. *Waste Manage. (Oxford)* 24 (1), 53–79. [https://doi.org/10.1016/S0956-553X\(03\)00038-2](https://doi.org/10.1016/S0956-553X(03)00038-2).
- de Marco Rodriguez, I., et al., 2001. Pyrolysis of scrap tyres. *Fuel Process. Technol.* 72 (1), 9–22. [https://doi.org/10.1016/S0378-3820\(01\)00174-6](https://doi.org/10.1016/S0378-3820(01)00174-6).
- Martínez, J.D., Murillo, R., et al., 2013. Demonstration of the waste tire pyrolysis process on pilot scale in a continuous auger reactor. *J. Hazard. Mater.* 261, 637–645. <https://doi.org/10.1016/j.jhazmat.2013.07.077>.
- Martínez, J.D., Puy, N., et al., 2013a. Waste tyre pyrolysis—A review. *Renew. Sustain. Energy Rev.* 23, 179–213.
- Martínez, J.D., et al., 2019. Carbon black recovery from waste tire pyrolysis by demineralization: production and application in rubber compounding. *Waste Manage. (Oxford)* 85, 574–584. <https://doi.org/10.1016/j.wasman.2019.01.016>.
- Martínez, J.D., Murillo Villuendas, R. and García, T. (2013) “Production of carbon black from the waste tires pyrolysis.”.
- Martínez, J.D., Gisele Jung, C., Bouysset, J.P., 2021a. Recovered carbon black: characteristics and properties in compounds. *Tire Waste and Recycling* 177.
- Menares, T., Herrera, J., Romero, R., Osorio, P., Arteaga-Pérez, L.E., 2020. Waste tires pyrolysis kinetics and reaction mechanisms explained by TGA and Py-GC/MS under kinetically-controlled regime. *Waste Manag* 102, 21–29. <https://doi.org/10.1016/j.wasman.2019.10.027>.
- Miranda, M., Pinto, F., Gulyurtlu, I., Cabrita, I., 2013. Pyrolysis of rubber tyre wastes: A kinetic study. *Fuel* 103, 542–552. <https://doi.org/10.1016/j.fuel.2012.06.114>.
- Mkhize, N.M., et al., 2016. Effect of temperature and heating rate on limonene production from waste tyre pyrolysis. *J. Anal. Appl. Pyrolysis* 120, 314–320. <https://doi.org/10.1016/j.jaap.2016.04.019>.
- Mkhize, N.M., et al., 2019. Influence of reactor and condensation system design on tyre pyrolysis products yields. *J. Anal. Appl. Pyrolysis* 143, 104683. <https://doi.org/10.1016/j.jaap.2019.104683>.
- Mooney, C.Z., et al., 1993. *Bootstrapping: A nonparametric Approach to Statistical Inference*. sage.
- Moulin, L., et al., 2017. Assessment of recovered carbon black obtained by waste tires steam water thermolysis: an industrial application. *Waste Biomass Valorization* 8 (8), 2757–2770. <https://doi.org/10.1007/s12649-016-9822-8>.
- Muenpol, S., Jitkarnka, S., 2016. Effects of Fe supported on zeolites on structures of hydrocarbon compounds and petrochemicals in waste tire-derived pyrolysis oils. *J. Anal. Appl. Pyrolysis* 117, 147–156. <https://doi.org/10.1016/j.jaap.2015.12.003>.
- Murphy, N., Bolder, I., 2020. LCA of RCb vs VCb. In: *Recovered Carbon Black Conference 2020. Recovered Carbon Black Conference*.
- Norris, C.J., Hale, M., Bennett, M., 2014. Pyrolytic carbon: factors controlling in-rubber performance. *Plast. Rubber Compos.* 43 (8), 245–256. <https://doi.org/10.1179/1743289814Y.0000000088>.
- Oboiren, B.O., North, B.C., 2017. A review of waste tyre gasification. *J. Environ. Chem. Eng.* 5 (5), 5169–5178. <https://doi.org/10.1016/j.jece.2017.09.057>.
- Okoye, C.O., et al., 2021. Manufacturing of carbon black from spent tyre pyrolysis oil – A literature review. *J. Clean. Prod.* 279, 123336. <https://doi.org/10.1016/J.JCLEPRO.2020.123336>.
- Orozco, S., et al., 2021. Pyrolysis of plastic wastes in a fountain confined conical spouted bed reactor: determination of stable operating conditions. *Energy Convers. Manage.* 229, 113768. <https://doi.org/10.1016/J.ENCONMAN.2020.113768>.
- Osayi, J.I., et al., 2018. Pyrolytic conversion of used tyres to liquid fuel: characterization and effect of operating conditions. *J. Mater. Cycles Waste Manage.* 1–13. <https://doi.org/10.1007/s10163-017-0690-5>.
- Oyedun, A., et al., 2012. Optimisation of particle size in waste tyre pyrolysis. *Fuel* 95, 417–424. <https://doi.org/10.1016/J.FUEL.2011.09.046>.
- Pakdel, H., Pantea, D.M., Roy, C., 2001. Production of dl-limonene by vacuum pyrolysis of used tires. *J. Anal. Appl. Pyrolysis* 57 (1), 91–107. [https://doi.org/10.1016/S0165-2370\(00\)00136-4](https://doi.org/10.1016/S0165-2370(00)00136-4).
- Palos, R., et al., 2021. Waste refinery: the valorization of waste plastics and end-of-life tires in refinery units. a review. *Energy Fuels* 35 (5), 3529–3557. <https://doi.org/10.1021/ACS.ENERGYFUELS.0C03918>.
- Parthasarathy, P., et al., 2016. Influence of process conditions on product yield of waste tyre pyrolysis—a review. *Korean J. Chem. Eng.* 33 (8), 2268–2286. <https://doi.org/10.1007/s11814-016-0126-2>.
- Peacocke, G.V.C. and Bridgwater, A.V. (1993) “Design of a novel ablative pyrolysis reactor.” in *Advances in thermochemical biomass conversion*. Springer, pp. 1134–1150.
- Pecho, J., et al., 2008. Reactive bed materials for improved biomass gasification in a circulating fluidised bed reactor. *Chem. Eng. Sci.* 63 (9), 2465–2476. <https://doi.org/10.1016/j.ces.2008.02.001>.
- Peterson, S.C., 2020. Coppiced biochars as partial replacement of carbon black filler in polybutadiene/natural rubber composites. *J. Compos. Sci.* 4 (4) <https://doi.org/10.3390/JCS4040147>.
- Piotrowska, K., et al., 2019. Assessment of the environmental impact of a car tire throughout its lifecycle using the Ica method. *Materials (Basel)* 12 (24), 4177. <https://doi.org/10.3390/ma12244177>.
- Pipilikaki, P., et al., 2005. Use of tire derived fuel in clinker burning. *Cem. Concr. Compos.* 27 (7–8), 843–847. <https://doi.org/10.1016/j.cemconcomp.2005.03.009>.
- Proch, F., Bauerbach, K., Grammenoudis, P., 2021. Development of an up-scalable rotary kiln design for the pyrolysis of waste tyres. *Chem. Eng. Sci.* 238, 116573. <https://doi.org/10.1016/j.ces.2021.116573>.

- Qu, W., et al., 2006. Pyrolysis of waste tire on ZSM-5 zeolite with enhanced catalytic activities. *Polym. Degrad. Stab.* 91 (10), 2389–2395. <https://doi.org/10.1016/j.polydegradstab.2006.03.014>.
- Raj, R.E., Kennedy, Z.R., Pillai, B.C., 2013a. Optimization of process parameters in flash pyrolysis of waste tyres to liquid and gaseous fuel in a fluidized bed reactor. *Energy Convers. Manage.* 67, 145–151.
- Rajesh, K., Dhanasekaran, D., Tyagi, B.K., 2013. Survey of container breeding mosquito larvae (Dengue vector) in Tiruchirappalli district, Tamil Nadu, India. *J. Entomol. Zool. Stud.* 1 (6), 88–91.
- Rezaian, J., Cheremisinoff, N.P., 2005. *Gasification technologies: a Primer For Engineers and Scientists*. CRC press.
- Rodríguez, E., et al., 2020. Scrap tires pyrolysis oil as a co-feeding stream on the catalytic cracking of vacuum gasoil under fluid catalytic cracking conditions. *Waste Manage. (Oxford)* 105, 18–26. <https://doi.org/10.1016/j.wasman.2020.01.026>.
- Rodríguez, E., Gutiérrez, A., Palos, R., Azkoiti, M.J., Arandes, J.M., Bilbao, J., 2019. Cracking of scrap tires pyrolysis oil in a fluidized bed reactor under catalytic cracking unit conditions. Effects of operating conditions. *Energy & Fuels* 33, 3133–3143. <https://doi.org/10.1021/acs.energyfuels.9b00292>.
- Roy, C., et al., 1997. Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber. *Fuel Process. Technol.* 50 (1), 87–103. [https://doi.org/10.1016/S0378-3820\(96\)01044-2](https://doi.org/10.1016/S0378-3820(96)01044-2).
- Roy, C., Chaala, A., Darmstadt, H., 1999. The vacuum pyrolysis of used tires: end-uses for oil and carbon black products. *J. Anal. Appl. Pyrolysis* 51 (1–2), 201–221. [https://doi.org/10.1016/S0165-2370\(99\)00017-0](https://doi.org/10.1016/S0165-2370(99)00017-0).
- San Miguel, G., Fowler, G.D., Sollars, C.J., 2002. Adsorption of organic compounds from solution by activated carbons produced from waste tyre rubber. *Sep. Sci. Technol.* 37 (3), 663–676. <https://doi.org/10.1081/SS-120001453>.
- Ruwona, W., Danha, G., Muzenda, E., 2019. A review on material and energy recovery from waste tyres. *Procedia Manufacturing* 35, 216–222.
- San Miguel, G., Fowler, G.D., Sollars, C.J., 1998. Pyrolysis of tire rubber: porosity and adsorption characteristics of the pyrolytic chars. *Ind. Eng. Chem. Res.* 37 (6), 2430–2435. <https://doi.org/10.1021/ie970728x>.
- San Miguel, G., Fowler, G.D., Sollars, C.J., 2003. A study of the characteristics of activated carbons produced by steam and carbon dioxide activation of waste tyre rubber. *Carbon N Y* 41 (5), 1009–1016. [https://doi.org/10.1016/S0008-6223\(02\)00449-9](https://doi.org/10.1016/S0008-6223(02)00449-9).
- Sathiskumar, C., Karthikeyan, S., 2019. Recycling of waste tires and its energy storage application of by-products—a review. *Sustain. Mater. Technol.* e00125. <https://doi.org/10.1016/j.susmat.2019.e00125>.
- Schmidt, H., et al., 2019. Pyrogenic carbon capture and storage. *GCB Bioenergy* 11 (4), 573–591. <https://doi.org/10.1111/gcbb.12553>.
- Senneca, O., Salatino, P., Chirone, R., 1999a. A fast heating-rate thermogravimetric study of the pyrolysis of scrap tyres. *Fuel* 78 (13), 1575–1581.
- Septien, S., et al., 2020. Effect of drying on the physical and chemical properties of faecal sludge for its reuse. *J. Environ. Chem. Eng.* 8 (1), 103652. <https://doi.org/10.1016/j.jece.2019.103652>.
- Sienkiewicz, M., et al., 2012. Progress in used tyres management in the European Union: a review. *Waste Manage. (Oxford)* 32 (10), 1742–1751. <https://doi.org/10.1016/j.wasman.2012.05.010>.
- Singh, R.K., et al., 2018. Pyrolysis of three different categories of automotive tyre wastes: product yield analysis and characterization. *J. Anal. Appl. Pyrolysis* 135, 379–389. <https://doi.org/10.1016/j.jaap.2018.08.011>.
- Sinn, H., Kaminsky, W., Janning, J., 1976. Processing of plastic waste and scrap tires into chemical raw materials, especially by pyrolysis. *Angew. Chem. Int. Ed. Engl.* 15 (11), 660–672. <https://doi.org/10.1002/anie.197606601>.
- Syamsiro, M., Dwicahyo, M.S., Sulistiawati, Y., Ridwan, M., Citrasari, N., 2019. Development of a rotary kiln reactor for pyrolytic oil production from waste tire in Indonesia. *IOP Publishing*, p. 12044.
- TR&R, 2021. *Pyrolyx AG Enters Bankruptcy. Tyre & Rubber Recycling*.
- Tudu, K., Murugan, S., Patel, S.K., 2016. Effect of diethyl ether in a DI diesel engine run on a tyre derived fuel-diesel blend. *J. Energy Inst.* 89 (4), 525–535. <https://doi.org/10.1016/j.joei.2015.07.004>.
- Ucar, S., et al., 2005. Evaluation of two different scrap tires as hydrocarbon source by pyrolysis. *Fuel* 84 (14–15), 1884–1892. <https://doi.org/10.1016/j.fuel.2005.04.002>.
- Unapumnuk, K., et al., 2008. Investigation into the removal of sulfur from tire derived fuel by pyrolysis. *Fuel* 87 (6), 951–956. <https://doi.org/10.1016/j.fuel.2007.05.036>.
- Uyumaz, A., et al., 2019. Production of waste tyre oil and experimental investigation on combustion, engine performance and exhaust emissions. *J. Energy Inst.* 92 (5), 1406–1418. <https://doi.org/10.1016/j.joei.2018.09.001>.
- Wang, C., Zhao, B., Tian, X., Wang, K., Tian, Z., Han, W., Bian, H., 2020. Study on the pyrolysis kinetics and mechanisms of the tread compounds of silica-filled discarded car tires. *Polymers (Basel)* 12, 810. <https://doi.org/10.3390/polym12040810>.
- Wang, J., Zhong, Z., Ding, K., Li, M., Hao, N., Meng, X., Ruan, R., Ragauskas, A.J., 2019. Catalytic fast co-pyrolysis of bamboo sawdust and waste tire using a tandem reactor with cascade bubbling fluidized bed and fixed bed system. *Energy Convers. Manage.* 180, 60–71. <https://doi.org/10.1016/j.enconman.2018.10.056>.
- Williams, P.T., 2013. Pyrolysis of waste tyres: a review. *Waste Manage. (Oxford)* 33 (8), 1714–1728. <https://doi.org/10.1016/j.wasman.2013.05.003>.
- Williams, P.T., Bottrill, R.P., Cunliffe, A.M., 1998. Combustion of tyre pyrolysis oil. *Process Saf. Environ. Prot.* 76 (4), 291–301. <https://doi.org/10.1205/095758298529650>.
- Williams, P.T., Brindle, A.J., 2002a. Catalytic pyrolysis of tyres: influence of catalyst temperature. *Fuel* 81 (18), 2425–2434.
- Williams, P.T., Brindle, A.J., 2002b. Fluidised bed catalytic pyrolysis of scrap tyres: influence of catalyst: tyre ratio and catalyst temperature. *Waste Manag. Res.* 20 (6), 546–555.
- Witpathomwong, C., et al., 2011. Improving light olefins and light oil production using Ru/MCM-48 in catalytic pyrolysis of waste tire. *Energy Procedia* 9, 245–251. <https://doi.org/10.1016/j.egypro.2011.09.026>.
- Xiang, Y., Fan, H., Liu, Z., 2020. Structural characteristics of silane-modified ground tyre rubber and high-temperature creep property of asphalt rubber. *Constr. Build. Mater.* 236, 117600. <https://doi.org/10.1016/j.conbuildmat.2019.117600>.
- Xu, Junqing, Yu, J., Xu, Jianglin, Sun, C., He, W., Huang, J., Li, G., 2020. High-value utilization of waste tires: A review with focus on modified carbon black from pyrolysis. *Sci. Total Environ.* 742, 140235. <https://doi.org/10.1016/j.scitotenv.2020.140235>.
- Yang, A.L.C., Ani, F.N., 2016. Controlled microwave-induced pyrolysis of waste rubber tires. *Int. J. Technol.* 7 (2), 314–322. <https://doi.org/10.14716/ijtech.v7i2.2973>.
- Yang, J., Tanguy, P.A., Roy, C., 1995. Heat transfer, mass transfer and kinetics study of the vacuum pyrolysis of a large used tire particle. *Chem. Eng. Sci.* 50 (12), 1909–1922. [https://doi.org/10.1016/0009-2509\(95\)00062-A](https://doi.org/10.1016/0009-2509(95)00062-A).
- Yaqoob, H., Teoh, Y.H., Jamil, M.A., Gulzar, M., 2021. Potential of tire pyrolysis oil as an alternate fuel for diesel engines: A review. *J. Energy Inst.* 96, 205–221. <https://doi.org/10.1016/j.joei.2021.03.002>.
- Yazdani, E., Hashemabadi, S.H., Taghizadeh, A., 2019. Study of waste tire pyrolysis in a rotary kiln reactor in a wide range of pyrolysis temperature. *Waste Manage. (Oxford)* 85, 195–201. <https://doi.org/10.1016/j.wasman.2018.12.020>.
- Zhang, X., et al., 2008a. Vacuum pyrolysis of waste tires with basic additives. *Waste Manage. (Oxford)* 28 (11), 2301–2310.
- Zhang, X., et al., 2018. Upgrading pyrolytic residue from waste tires to commercial carbon black. *Waste Manag. Res.* 36 (5), 436–444. <https://doi.org/10.1177/0734242X18764292>.
- Zhou, J., et al., 2006. Surface modification of pyrolytic carbon black from waste tires and its use as pigment for offset printing ink. *Chin. J. Chem. Eng.* 14 (5), 654–659. [https://doi.org/10.1016/S1004-9541\(06\)60130-4](https://doi.org/10.1016/S1004-9541(06)60130-4).
- RJA (2020) "Tyre pyrolysis: an epic fail or a recycling nirvana?".
- Jahirul, M.I., Hossain, F.M., Rasul, M.G., Chowdhury, A.A., 2021. A Review on the Thermochemical Recycling of Waste Tyres to Oil for Automobile Engine Application. *Energies* 2021, Vol. 14, Page 3837 14, doi:/3837./10.3390/en14133837.
- Dabic-Miletic, S., Simic, V., Karagoz, S., 2021. End-of-life tire management: a critical review. *Environ. Sci. Pollut. Res.* 2021 2848 28, 68053–68070. doi:/10.1007/s11356-021-16263-6.