



Consecutive recovery of recovered carbon black and limonene from waste tyres by thermal pyrolysis in a rotary kiln

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ABSTRACT

End of life tyres are one of the most abundant and least recycled waste streams. Material recovery processes that accommodate for the complexity and heterogeneity of waste tyres, such as pyrolysis, require urgent development. Examples of recycled tyre pyrolysis products include recovered carbon black (RCb), a recycled filler, and limonene, a solvent, although investigations reporting the recovery of both are limited. In this study the pyrolysis of waste tyres was investigated in a batch rotary kiln under varying conditions (temperature, gas flow, sample mass). Characterisation analysis was then applied to selected samples of RCb (BET surface area, transmissibility of toluene extract, proximate analysis) and tyre pyrolysis oil (yield, limonene content, FTIR). The best RCb (77.7 m²/g, 0.2% volatile matter, 17.0% ash, 94.8% transmissibility of toluene extract) was produced at 550 °C with a high ratio of purge gas flow (2000 mL/min) to rubber sample mass pyrolysed (100 g), minimising the recondensation of tarry volatiles on the RCb. The highest oil and limonene yield (38.4% and 17.4 g/kg waste tyres respectively) was produced at a temperature of 550 °C with a low ratio of purge gas (400 mL/min) to rubber sample pyrolysed (200 g), as these conditions prevented the decomposition of limonene to less valuable products and improved the oil trap condensation efficiency. These findings demonstrate the importance of pyrolysis processing conditions when considering the consecutive production of RCb and solvents from waste tyre pyrolysis, which shows significant future potential to valorise waste tyres, incentivising recycling.

1. Introduction

Over 1 billion tyres are produced and discarded annually (Goldstein, 2020; Ruwona et al., 2019). Due to their durability, waste tyres impose a large environmental burden (Sathiskumar and Karthikeyan, 2019). Tyre fires and disease-spreading insects have been associated with tyre dumps (Jimoda et al., 2018; Rajesh et al., 2013). Due to their flammability and non-biodegradability, tyres are unsuitable for disposal in landfill sites (EU, 1999; Forrest, 2019). Use of waste-tyres as a supplementary fuel in combustion systems is common yet achieves poor value-return from a material and energy-intensive product. Over 300 kg of CO₂ is released during the production of a single tyre, therefore the emissions factor of tyre combustion is 85 g CO₂/MJ, which is only 11% lower than coal (Usón et al., 2013; Piotrowska et al., 2019). Due to their heterogeneity, complexity, and the thermodynamic characteristics of vulcanisation, waste tyres are challenging to recycle using depolymerisation techniques such as devulcanisation (Asaro et al., 2018; Sabzekar et al., 2015). This necessitates the development of alternative material recycling techniques.

Pyrolysis is defined as the thermochemical breakdown of organic waste material by energisation with heat, microwaves (Foong

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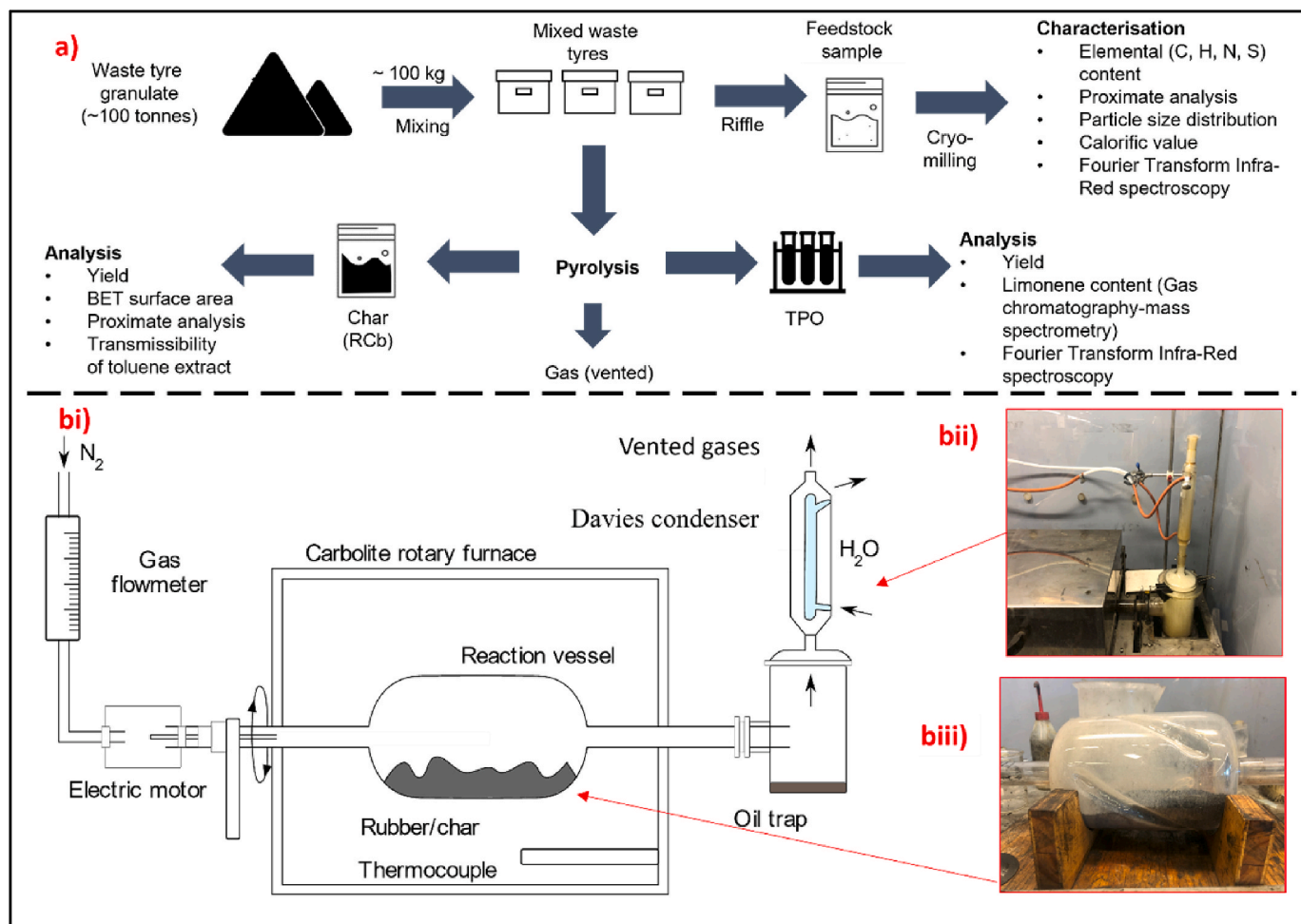


Fig. 1. a) Schematic of the study method. bi) Pyrolysis furnace and oil trap used. bii) The volatiles condensation system. biii) Vessel loaded with the rubber granulate.

et al., 2020), or ultrasound in the absence of oxygen. Although pyrolysis is an effective treatment mechanism for biomass (Foong et al., 2020), sewage sludge (Krueger et al., 2020, 2021), and municipal solid waste (Mahari et al., 2021), it is particularly suitable for waste tyres as it can effectively separate primarily carbon black (Cb) derived carbon (which produces char after pyrolysis) from the rubber and textile (from the reinforcing cord) derived carbon compounds (which produce oil and gas), enabling more effective recovery of both product streams. Potential applications for tyre pyrolysis char include activated carbons (Antonioni et al., 2014; Doja et al., 2022; Jones et al., 2021; Kuśmierik et al., 2021a, 2021b), catalysts (Al-Rahbi and Williams, 2016; Zhou et al., 2019), and battery anodes (Li et al., 2016; Kumar and Sharma, 2018). Tyre-derived pyrolysis char contains a high proportion of carbon black, a material with a high surface area and surface activity, which can retail for up to \$1000/tonne when destined for use as a recycled filler in new polymers, including tyres, as recovered carbon black (RCb) (Anjum et al., 2019; Martinez et al., 2021; Moulin et al., 2017). The characteristics of Cb and RCb differ resulting in the need for new testing and comparison procedures that are currently being addressed by the ASTM D.36 committee (Koury, 2018). Despite the potential greenhouse gas emissions savings offered by RCb, optimal conditions for its production within a tyre pyrolysis system remain poorly characterised (Martinez et al., 2021) resulting in product heterogeneity. Residual volatile matter (VM) is particularly problematic and should be minimised as it significantly reduces both the surface area and surface activity of the RCb, which inhibits its applicability in recycled polymers (Martínez et al., 2013).

Tyre-derived volatiles consist of a mixture of liquid (C_4 – C_{20} hydrocarbons) and gas-based (C_1 – C_4 hydrocarbons, CO , H_2 , CO_2 , and sulphur containing compounds) products (Elbaba et al., 2011). For very heterogeneous or contaminated wastes, the gas fraction can be easier to process and valorise than the oil fraction through techniques such as steam or catalytic reforming (Foong et al., 2021). Nevertheless due to the high energy density and proportion of valuable products, high pyrolysis oil yields are usually viewed preferentially to high gas yields after tyre pyrolysis (Bowles and Fowler, 2022). Most of the research relating to condensable tyre pyrolysis oil (TPO) has been focussed on its use as a fuel (Arya et al., 2020; Dick et al., 2020; Jahirul et al., 2021; Yaqoob et al., 2021; Zhang et al., 2021), which can be considered a partial biofuel due to natural rubber components that are incorporated during tyre manufacture. TPO can be sub-categorised to lighter solvents, and heavier tar-like products. The heavier compounds can be refined further by processes such as hydrogenation or fluid-catalytic cracking to produce a range of recycled petrochemical products (Kumaravel et al., 2016; Palos et al., 2021). Alternatively, the heavier fractions can be processed to produce TPO-derived carbon blacks (Okoye et al., 2021). The valuable solvents in TPO, i.e., benzene, toluene, xylene, ethylbenzene and rubber monomers such as isoprene, should be separated prior to these refining steps. Commonly, the most valuable and abundant light solvent in TPO is limonene, a dipentene traditionally derived from citrus fruits (Januszewicz et al., 2020a). Limonene has potential applications as a solvent in cleaning products, for plasticizers, and in paints, lacquers, fragrances, or as a pharmaceutical product (Januszewicz et al., 2020a; Sadi et al., 2020). It is a valuable product and its yield from tyre pyrolysis should be maximised.

Investigations reporting the combined production of RCb and limonene from waste tyres remain limited (Mkhize et al., 2019). Previous literature analysis has highlighted the effectiveness of rotary kilns to produce high oil yields and low-VM char by utilising effective mixing combined with a high gas to solid contact area, promoting volatilisation (Bowles and Fowler, 2022). In primary literature, char VM content, oil yield, and oil limonene content has been sparsely reported from tyre pyrolysis in rotary kilns. Li et al. utilised a continuous rotary kiln to produce oil yields of up to 45.1%, with 5.4 wt% limonene, but RCb VM content remained high (>5 wt%), even at higher pyrolysis temperatures (Li et al., 2004). Galvagno et al. also produced high oil yields (~38%) in their rotary kiln, but also reported high char VM contents at higher pyrolysis temperatures (Galvagno et al., 2002). Antonioni et al. produced a very high oil yield (~52%) in their rotary kiln, but did not provide data on the RCb volatiles content (Antonioni and Zabaniotou, 2015). Xu et al. recently analysed detailed information regarding the RCb characteristics from their continuous rotary kiln reactor, but the RCb also had a high volatiles content (11%) (Xu et al., 2021). There is thus a requirement for an investigation regarding the main effects of how process conditions affect the production of low-VM recovered carbon black, whilst also producing maximum tyre pyrolysis oil, and limonene yields during pyrolysis in a rotary kiln reactor.

The aim of this work was thus to systematically analyse how tyre pyrolysis highest heating temperature, sample mass, and gas flow affect the combined production of oil, limonene, and RCb within the same reactor. This would increase the profitability of tyre recycling, valorising waste and would contribute towards a circular tyre lifecycle.

Table 1

Experimental conditions deployed in this study. Each condition was repeated three times, with thirty runs in total. Conditions 1–8 were required for the 2^3 factorial design which allowed for a systematic analysis of the main effects of highest heating temperature (HHT), nitrogen gas flowrate (N_2 -F) and rubber sample pyrolysed (SM) on oil and char recoverability. Conditions 9 and 10 were added subsequently to assess the effect of increasing the HHT further.

Condition	HHT [°C]	N_2 -F [mL/min]	SM [g]
1	450	400	100
2	450	400	200
3	450	2000	100
4	450	2000	200
5	550	400	100
6	550	400	200
7	550	2000	100
8	550	2000	200
9	650	2000	100
10	650	400	200

2. Methodology

Fig. 1a schematically illustrates the study method. Representatively-sampled truck and car tyre granulate (50:50) sourced from an industrial facility in Grimsby, UK, was analysed for carbon, hydrogen, nitrogen, and sulphur (CHNS) content (MEDAC Ltd., Surrey, UK), particle size (using a QICPIC particle size analyser), calorific value (ASTM 70 D5865M – 19 (ASTM, 2019) using a 6100 Calorimeter by Parr Instrument Company, USA) and by thermal and proximate analysis (ASTM D36.10 AC442 on a Rheometric Scientific STA-1500 thermogravimetric analyser). A Hitachi TM4000Plus Tabletop SEM was used to image the rubber crumb particles. Fourier Transform Infra-Red (FTIR) spectra (ASTM E 1252 – 98) were gathered on a Nicolet 6700 FT-IR Spectrometer (Thermo Fisher Scientific, USA) within a wavenumber range of $4000\text{--}500\text{ cm}^{-1}$ using a diamond ATR-crystal with internal correction for background signal.

The rotary pyrolysis kiln (a modified Carbolite HTR 11/150 laboratory-scale furnace) used in this investigation is illustrated in Fig. 1bi. The loaded 3.2 L furnace (see Fig. 1biii) had internal riffling to potentiate mixing and was heated at a rate of $16.5\text{ }^{\circ}\text{C}/\text{min}$ to the desired HHT (see Table 1). It was rotated at a speed of 10 rpm by using nitrile seals and high temperature grease to ensure an inert atmosphere was maintained within the kiln. Volatiles were purged from the system via flowing N_2 gas, whilst the carbonised char remained within the reaction vessel. Heavier volatiles were condensed within an oil trap (see Fig. 1bii) which had a volume of 2 L and was attached to a Davies Condenser cooled with water at $8\text{ }^{\circ}\text{C}$. The temperature of the oil trap during pyrolysis was measured by inserting a K-type thermocouple wire down the condenser. The gas stream outflow was vented within a fume cupboard. Yields were calculated from the mass difference between the vessel reactants and the oil trap contents.

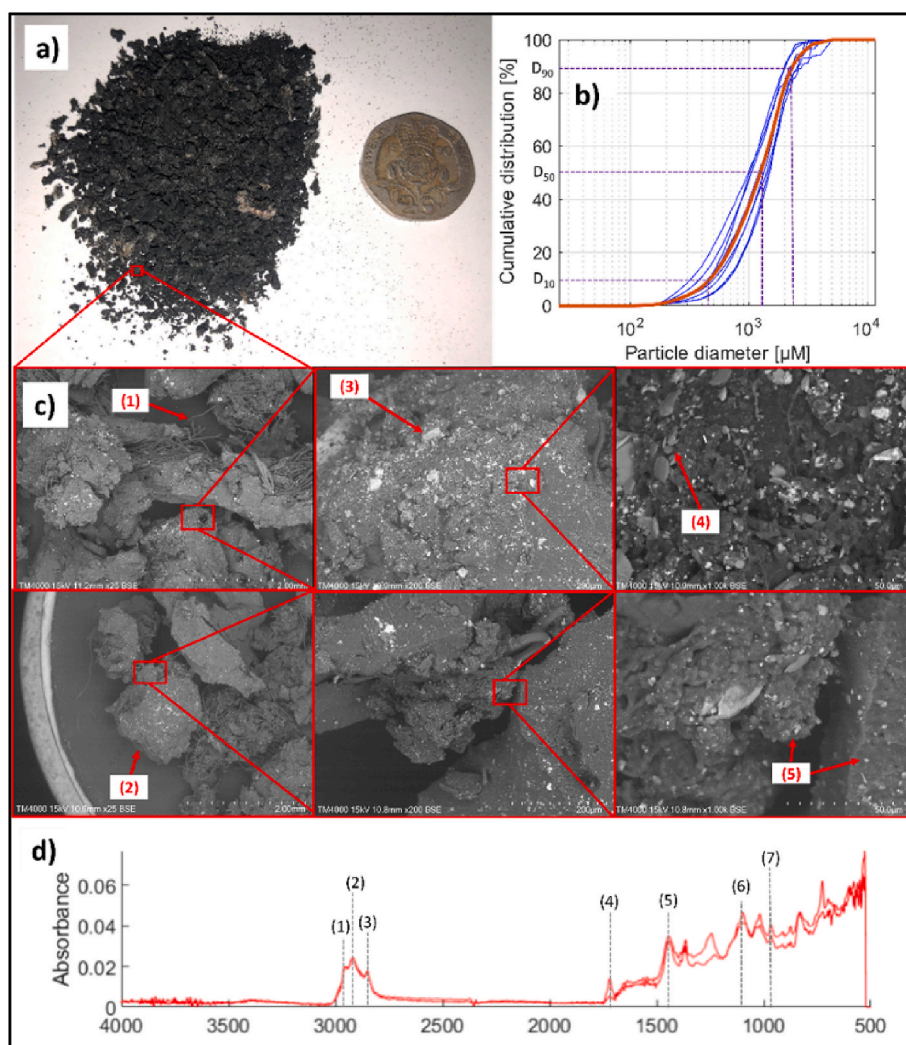


Fig. 2. a) Photograph of sample with scale reference. b) Cumulative particle size distribution from QICPIC. c) SEM images of the rubber crumb sample where (1): textile cord, (2): rubber crumb, (3),(4): larger inorganic (silica) and (5): smaller inorganic fragment, possibly Zn, S, or metal-based compounds. d) FTIR spectrum of the rubber granulate with key characteristic peaks highlighted. (1): CH_3 stretching, (2): CH_2 stretching, (3): CH stretching, (4): $\text{C}\equiv\text{C}$ or $\text{C}=\text{O}$ stretching, (5): Styrene comonomer, (6): $\text{S}-\text{O}$, (7): Butadiene comonomer.

Producing low (<1%) VM char (RCb) and a high oil yield has recently been identified as the primary aims of a commercial tyre pyrolysis system (Bowles and Fowler, 2022). A 2³ full-factorial design (see Appendix A and Conditions 1–8 in Table 1) was therefore deployed initially to provide a systematic analysis of the major effects influencing RCb VM content and oil yield during pyrolysis and to allow for a three-way ANOVA to be used to determine any effects and their possible interactions. The conditions that produced the lowest VM char and the highest oil yield were then subjected to further analysis. Extra conditions (see Conditions 9 and 10 in Table 1) were subsequently added to further analyse the effects of increasing the HHT on the RCb properties and the limonene yield. Heterogeneity in feedstock properties and process performance was expected to cause inherent variation in the results attained, which are traits attributable to most waste processing systems. This variation was accounted for by repeating each run three times with the mean and standard deviation presented as representations of the best estimator and uncertainty, respectively.

Selected char (RCb) samples were further characterised by proximate analysis, FTIR, SEM, BET surface area (ASTM D6556-19 on a Quantachrome Corp Autosorb iQ 3), and for transmissibility of toluene extract to assess levels of contaminant residues on the RCb surface (ASTM D1618 – 18 using a M550 double beam scanning UV/Visible spectrophotometer from Spectronic CamSpec). Commercial carbon blacks N220, N550 and N772 were analysed for reference purposes. Limonene content within the TPO was determined by GC-MS (CLARUS 500 GC/MS, PerkinElmer, USA) fitted with and an RXi-5MS 30 m long, 0.25 mm internal diameter fused-silica capillary column of 0.25 µm film thickness (Restek) calibrated with suitable standards (Flourochem, UK). Ethanol was used as a solvent, and a 50:1 split ratio was applied. 1.0 µL of sample was injected at an initial temperature of 40 °C for 1 min. The temperature was then ramped to 200 °C at 30 °C/min and held for 5 min. All statistical functions were performed using inbuilt functions in MATLAB (MathWorks, USA) and JMP Pro (JMP, USA) software.

3. Results

3.1. Feedstock characterisation

The feedstock (see Fig. 2a) had been mechanically granulated to a particle diameter of 1.5 ± 0.9 mm (see Fig. 2b) prior to analysis. SEM (see Fig. 2c) revealed several heterogeneities within the rubber, including textiles and a range of inorganic fragments. The high ash content ($6.5 \pm 0.6\%$) was attributed to a combination of inorganic additives used in the tyre composition (silica, Zn compounds) and from road and soil residue on the surface of the waste tyres (Banar et al., 2015). The FTIR spectra of the rubber sample (Fig. 2d) were indicative of organic groups associated with styrene butadiene (artificial rubber) and sulphur from the vulcanisation stage of tyre manufacture, which concurs with the high sulphur content observed in the elemental analysis (see Table 2). The high carbon ($82.3 \pm 1.1\%$) and fixed carbon ($28.4 \pm 0.3\%$) content could have been attributed to a high carbon black content in the feedstock. C=O groups in the FTIR spectra may have been attributable to oxygenated functional groups on the rubber surface and also the carbon black within it. The sample also had a high calorific value and volatile matter content, suggesting high volatile (oil and gas) and energy yields are attainable from the pyrolysis of this rubber granulate. Expected volatile matter (VM)-free char yields can be approximated by Fixed Carbon + Ash = $34.9 \pm 0.9\%$ (Bowles and Fowler, 2022).

3.2. Primary and secondary pyrolysis: influencing parameters

The effects of highest heating temperature (HHT), gas flow (N₂-F), and rubber sample mass pyrolysed (SM) on primary pyrolysis (RCb-VM content) and secondary pyrolysis (oil yield) are shown in Fig. 3a and b, respectively. A 3-way ANOVA was performed to determine the relationship between dependent and independent variables (see Table 3).

The results suggested that HHT is the dominant determinant of RCb-VM content (shown by the high F ratio in Table 3), followed by N₂-F, and then SM. The ANOVA analysis suggested that interactions may have been present between the N₂-F and HHT, and between the N₂-F and SM. Fig. 3a shows that SM and N₂-F exerted a greater effect on RCb-VM at a lower HHT. For example, for a SM of 200 g, increasing the N₂-F from 400 to 2000 mL had an increased effect on the resultant RCb-VM at a HHT of 450 °C ($37.4 \pm 4.0\%$ vs $26.5 \pm 3.8\%$) than for a HHT of 550 °C ($4.2\% \pm 1.1\%$ vs $2.1 \pm 1.5\%$). This suggests that SM and N₂-F become increasingly important with decreasing HHT. Gas kinetics are critical for the transport of tarry-volatilised compounds away from the char to the oil trap. High SM: N₂-F ratios would limit gas: solid contact areas, preventing effective mobilisation of tarry compounds to the oil trap, causing potential recondensation onto the char. It can be seen from Fig. 3a that the RCb with the lowest VM content ($0.2 \pm 0.3\%$) was pyrolysed at the higher HHT value (550 °C) in combination with a low sample mass (100 g) to gas flow (2000 mL/min) ratio. These chars were subjected to further analysis in Section 3.3.

Oil yield was also significantly affected by all three independent variables. In addition, the ANOVA suggested statistically significant associations between N₂-F and HHT, and N₂-F and SM. An increase in the SM from 100 to 200 g improved oil yield by around 4–8% for both HHTs and N₂-Fs analysed, whereas N₂-F did not significantly affect oil yield at 450 °C HHT and 100 g SM. This suggests that 400 mL/min of nitrogen was sufficient to mobilise the volatile components to the oil trap at 450 °C when 100 g of SM was pyrolysed. When the rubber sample mass was increased to 200 g during pyrolysis at 450 °C, more oil was reported for a N₂-F of 2000 mL/min ($25.1 \pm 0.5\%$) when compared to 400 mL/min ($21.5 \pm 1.5\%$) suggesting that higher gas flows are required to mobilise the

Table 2

Proximate and total elemental analysis of the tyre feedstock. C = carbon, H = hydrogen, N = nitrogen, S = sulphur, VM = volatile matter, FC = fixed carbon, ash = inorganics and CV = calorific value.

C [%]	H [%]	N [%]	S [%]	VM [%]	FC [%]	Ash [%]	CV [MJ/kg]
82.3 ± 1.1	14.8 ± 0.4	1.2 ± 0.1	3.1 ± 0.4	65.6 ± 0.4	28.4 ± 0.3	6.5 ± 0.6	35.0 ± 0.4

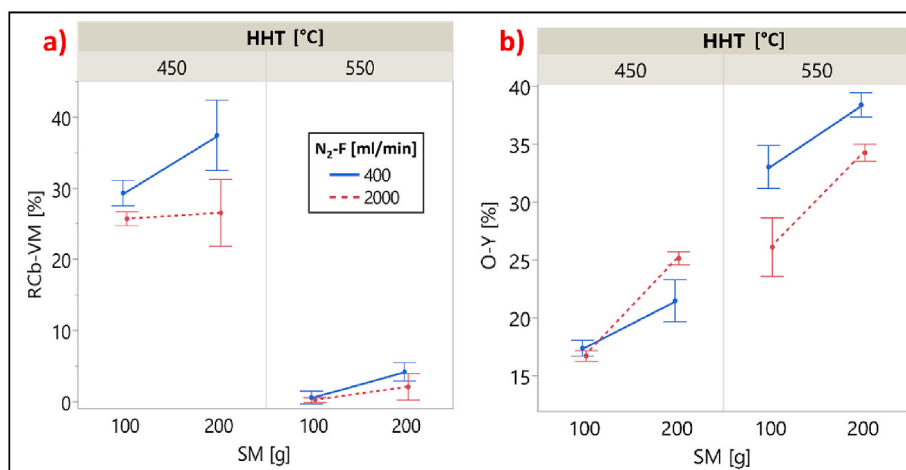


Fig. 3. The effect of HHT, nitrogen gas flow rate (N₂-F) and mass of rubber sample (SM) on a) RCB VM content and b) oil yield (O-Y). The graphs have been sub-categorised according to HHT.

Table 3

Results for the 3-way ANOVA. HHT = highest heating temperature. N₂-F = nitrogen gas flow. SM = sample mass. F ratio = ratio of mean square values. Bold values indicate significant effects ($\alpha = 0.05$).

	Source	Sum of Squares	F Ratio	Prob > F
RCb-VM	HHT	4847	679.3	<.0001
	N ₂ -F	109.4	15.3	<0.001
	SM	82.6	11.6	0.003
	HHT*N ₂ -F	54.7	7.7	0.012
	N ₂ -F*SM	32.9	4.6	0.046
	HHT*SM	5.1	0.7	0.409
Oil yield	HHT	1010.9	550.5	<.001
	SM	262.1	142.7	<.001
	HHT*N ₂ -F	76.0	41.4	<.001
	N ₂ -F	25.6	13.9	0.015
	N ₂ -F*SM	20.0	10.9	0.004
	HHT*SM	0.4	0.2	0.633

increased level of tarry volatile matter to the oil trap, and to avoid its recondensation onto the RCb. The highest oil yields ($38.4 \pm 0.9\%$) were recorded for a HHT of 550°C , a SM of 200 g, and a gas flow of 400 mL/min. These TPO samples were subjected to GC/MS analysis for limonene content, as detailed in Section 3.4.

3.3. Analysis of recovered carbon black (RCb)

Fig. 4 shows the characteristics of the RCb produced from Conditions 3 ("RCb-450 °C"), 7 ("RCb-550 °C") and 9 ("RCb-650 °C") (see Table 1). Volatile matter content, ash content, BET surface area and the transmissibility of toluene extract were tested, with Cb-N772, Cb-N550, and Cb-N220 provided for reference. Increasing the HHT from 450 to 550 °C significantly improved volatilisation, as RCb-550 °C had a volatile matter content that was >99% lower ($0.2 \pm 0.3\%$) than RCb-450 °C ($25.5 \pm 0.9\%$), and equivalent to commercial N550 carbon black (0.1%). This volatilisation caused improvements in other properties of RCb-550 °C, such as an increased BET surface area ($77.7 \pm 2.3 \text{ m}^2/\text{g}$ as opposed to $13.0 \pm 2.0 \text{ m}^2/\text{g}$ in RCb-450 °C), which was greater than the surface area of the N550 grade virgin carbon blacks ($42.4 \pm 0.9 \text{ m}^2/\text{g}$) though lower than N220 ($115.7 \pm 0.8 \text{ m}^2/\text{g}$).

RCb-550 °C also had an increased transmissibility of toluene extract ($94.8 \pm 0.8\%$). An increase in the HHT from 550 to 650 °C was associated with negligible changes in VM content and BET surface area although decreased the transmissibility of toluene extract very slightly ($93.2 \pm 0.2\%$). This suggests that more carbonaceous residues, which are not volatilizable at 550 °C under nitrogen in the proximate analysis test, may have formed from coking during pyrolysis at a highest heating temperature of 650 °C. A higher transmissibility of toluene extract was recorded for N550 ($99.0 \pm 0.7\%$) and N220 ($99.3 \pm 0.5\%$) grade virgin carbon blacks, suggesting that they contained fewer toluene-extractable contaminants than the RCbs produced in this study.

3.4. Analysis of limonene in tyre pyrolysis oil

Tyre pyrolysis oil (TPO) from Conditions 2 ("TPO-450 °C"), 6 ("TPO-550 °C"), and 10 ("TPO-650 °C") (see Table 1) were further characterised for limonene content. Fig. 5 shows ai) the chromatogram of the TPO-550 °C sample, and aii) the limonene peak mass spectrum. The presence of limonene is also evident in the FTIR spectrum of Fig. 5b, which provided a 27.49% match with DL-limonene (HR Aldrich Hydrocarbons database). Table 4 describes the TPO yields and limonene contents. TPO-450 °C contained the highest

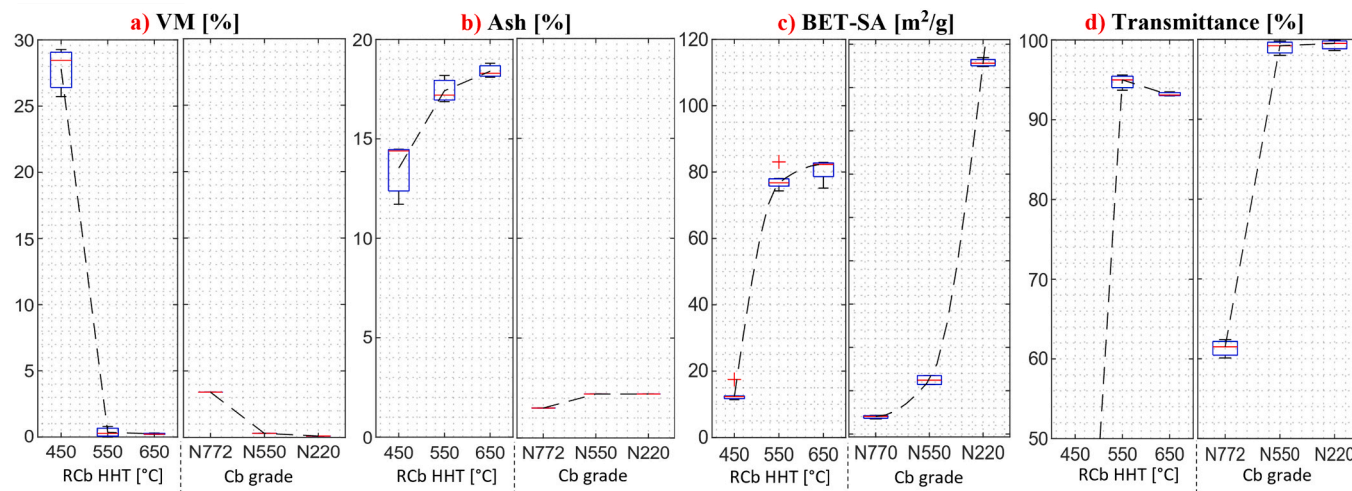


Fig. 4. Boxplots showing the effect of HHT on selected RCb properties: a) VM content, b) ash content, c) BET-surface area (BET-SA), d) transmittance of toluene extract. Commercial carbon blacks (N772, N550, and N220) are provided as reference materials. SM = 100 g, N₂-F = 2000 ml/min.

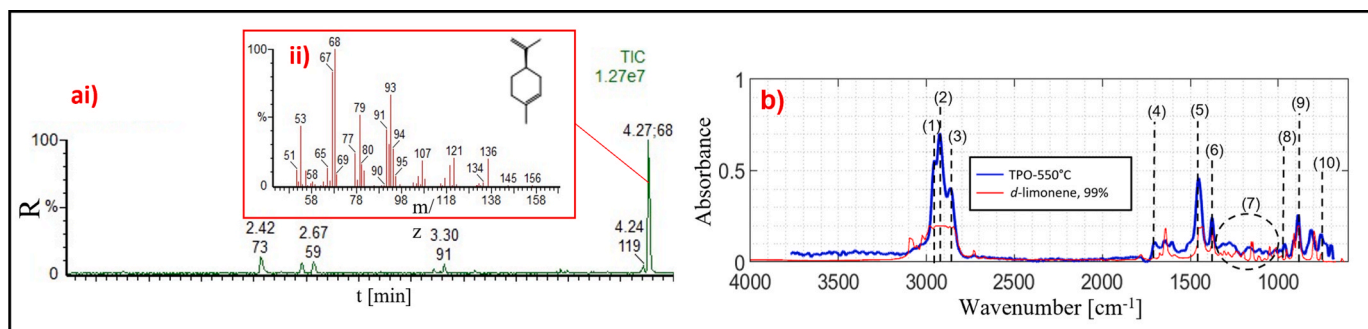


Fig. 5. ai) chromatogram from TPO-550 °C with aii) mass chromatogram of limonene. TIC: total electron count. b) FTIR spectrum of TPO-550 °C, with (1): CH_3 stretching, (2): CH_2 stretching, (3): CH stretching, (4): $\text{C}=\text{C}$ stretching, (5): CH_2 bending, (6): CH_3 bending or $\text{C}=\text{O}$ formation (7): Oxygen and sulphur containing functional groups (8): CH (butadiene group), (9),(10): geminal di-substituted and tri-substituted alkenes (Singh et al., 2019).

proportion of limonene (7.2 ± 0.4 wt% of TPO), and was of broadly similar recoverability (15.4 ± 1.8 g/kg steel free waste tyres) to TPO-550 °C (17.4 ± 0.7 g/kg). At higher (650 °C) pyrolysis temperatures, TPO limonene content decreased significantly (2.3 ± 0.5 wt %) suggesting thermal degradation. This considerably reduced the recoverability of limonene as a proportion of waste tyre feedstock at a HHT of 650 °C when compared to 550 °C.

4. Discussion

4.1. Effect of gas flow upon the system

The basic oil trap used in this study provided an insight into the dependence of the ratio of gas flow (N_2 -F) to sample mass (SM) in a pyrolysis system on the recoverability of RCb and lighter oil-based compounds such as limonene from waste tyre pyrolysis. The residence time (τ) of the volatiles (v) in the kiln ($\tau_{v,k}$) should be short to remove as much tarry VM from the tyre char as possible whilst minimising the secondary pyrolysis of volatilised oil-based compounds, particularly the valuable solvents (see Fig. 6b). The volatiles residence time in the oil condensation system ($\tau_{v,c}$) should be adequate to facilitate maximum condensation of lighter solvents such as limonene (see Fig. 6a).

$\tau_{v,k}$ and $\tau_{v,c}$ can be predicted from Equation (1).

$$\tau_{v,s} = \frac{V_s}{dV_{v,s}/dt} \quad (1)$$

where $\tau_{v,s}$ = the volatile residence time in a subunit (s) of the pyrolysis process, where s can be the kiln (k) or oil condensation trap (c), $dV_{v,s}/dt$ = the volume of volatiles released per unit of time in the kiln or the oil trap, V_s = the volume of the subunit, such as the kiln (3.2 L) or condensation trap (2 L). $dV_{v,s}/dt$ can be predicted from Equation (2) using the ideal gas law re-arranged for the determination of volume.

$$\frac{dV_{v,s}}{dt} = \frac{\frac{dn}{dt} RT_s}{P} \quad (2)$$

Where dn/dt = the number of moles of gas released per unit of time from both the volatile matter in the rubber and from the introduction of nitrogen gas, R = the universal gas constant, T_s = temperature in the pyrolysis process subunit (kiln or condensation trap), and P = pressure (101325 Pa). dn/dt can be predicted from feedstock and pyrolysis processing data according to Equation (3).

$$\frac{dn}{dt} = \frac{F_{VM}S}{M_{VM} t_{pp}} + \frac{G}{V_{g,STP}} \quad (3)$$

Where F_{VM} = the VM content fraction of the rubber (65.6%), S = sample mass pyrolysed (SM), M_{VM} = molecular weight of the volatile matter fraction, t_{pp} = time for primary pyrolysis to complete, G = the flowrate of gas applied to keep the atmosphere inert (N_2 -F), and $V_{g,STP}$ = the volume of 1 mol of gas at STP (22.4 L), which corresponded approximately to the inflow conditions for the nitrogen carrier gas. Equations (1)–(3) therefore can be rearranged and simplified to give Equation (4).

$$\tau_{v,s} = \frac{V_s P t_{pp} M_{VM} V_{g,STP}}{R T_s V_{g,STP} F_{VM} S + R T_s M_{VM} G t_{pp}} \quad (4)$$

It has been previously reported that the average molecular weights of tyre pyrolysis gas and oil are approximately 7.9 (Bianchi et al., 2014) and 250 (Williams and Taylor, 1994) g/mol, respectively. If it is assumed that the 65.6% volatile matter content of the tyre rubber (F_{VM}) produces oil and gas-based compounds during pyrolysis at a 3:1 ratio, then the M_{VM} would have a value of approximately 165 g/mol. Differential thermogravimetric curves suggest that the majority of tyre rubber primary pyrolysis occurs between 350 °C and 550 °C (Kordoghli et al., 2017). This would result in a primary pyrolysis reaction time (t_{pp}) of ~12 min for a heating rate of 16.5 °C/min as applied in this study. If it is further assumed that T_k = 450 °C (the midpoint of the range of primary pyrolysis), T_c = 50 °C, and that the gases behave in an ideal manner, are perfectly mixed, and are in steady state, Equations (1)–(4) can be used to provide an approximate estimate of $\tau_{v,s}$. When 100 g of tyre granulate is pyrolysed, predicted $\tau_{v,k}$ and $\tau_{v,c}$ values were 26 s and 37 s, respectively when the higher N_2 gas flow rate (2000 mL/min) was used and 63 s and 89 s, respectively, when the lower gas flow rate (400 mL/min) was used.

The higher $\tau_{v,c}$ would have caused stratification of the heavier gaseous compounds below the lighter ones when the lower N_2 -F gas flow rate was selected (see Fig. 6a) which did not occur at the higher gas flow rate (Fig. 6b). The recirculation of a portion of the pyrolysis gas would reduce the volatile residence time in the kiln without the requirement for an external inert carrier gas (such as N_2) in a full commercial system. The recirculation of tarry volatiles, however, would not be preferable due to the risk that they would

Table 4

TPO yield and limonene recoverability from waste tyres.* = as a proportion of steel-free waste tyre feedstock. SM = 200 g, N_2 -F = 400 mL/min.

	TPO yield [%]	Limonene content [% of TPO]	Limonene recovered [g/kg feedstock]	Limonene recoverability* [%]
TPO-450 °C	21.5 ± 1.5	7.2 ± 0.4	15.4 ± 1.8	1.5 ± 0.2
TPO-550 °C	38.4 ± 0.9	4.5 ± 0.1	17.4 ± 0.7	1.7 ± 0.1
TPO-650 °C	37.9 ± 0.8	2.3 ± 0.5	8.7 ± 2.0	0.9 ± 0.2

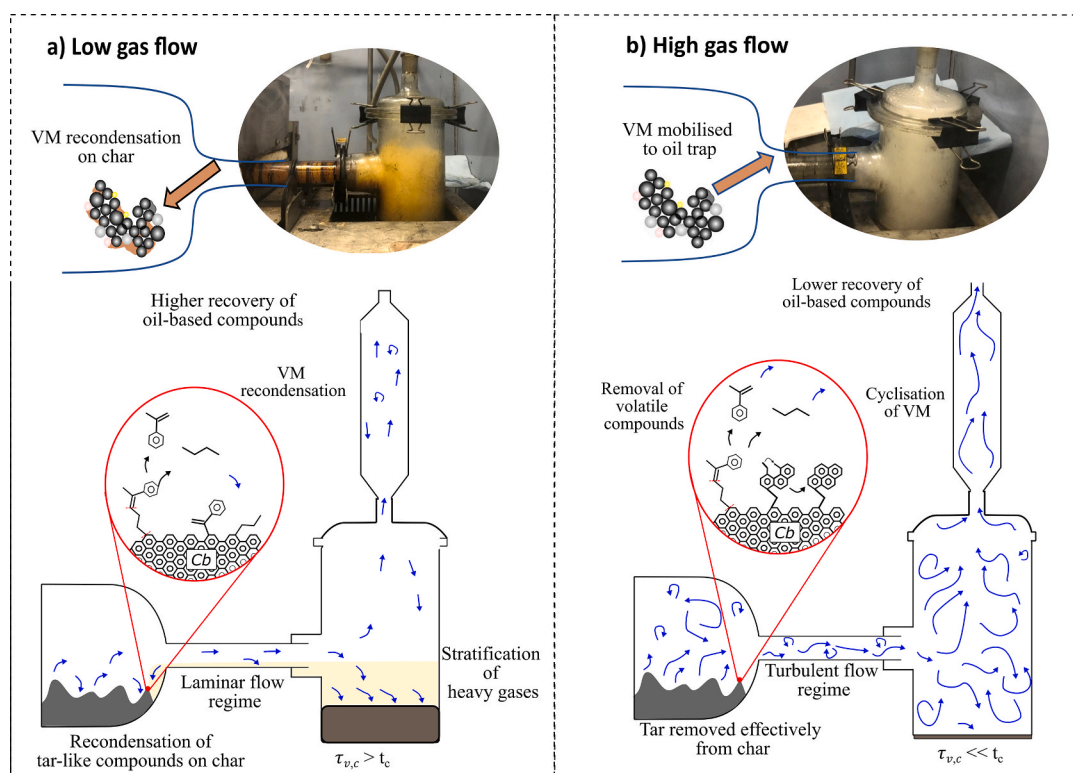


Fig. 6. Volatile kinetics at a) low gas flow (400 mL/min) and b) high gas flow (2000 mL/min). t_c = time required for condensation of oil-based volatiles to occur.

recondense on the RCb, reducing its quality. In a commercial plant, this stratification may be beneficial as it could allow the oil condensation system to be positioned below the kiln; this would encourage heavier, tar like volatiles to sink to the oils trap whilst lighter volatiles could be recirculated to the kiln to maintain the oxygen-free atmosphere.

The ratio of $\tau_{v,k}$ to $\tau_{v,c}$ (which was ~ 0.7 in this study) would ideally be as low as possible to improve RCb and limonene recovery from waste tyre pyrolysis and is related to the temperature profile of the volatiles (i.e., T_k and T_c). A lower T_c in the oil trap would require a higher energy demand to cool the volatiles but would require a lower $\tau_{v,c}$ for effective condensation of oil-based compounds when compared to a condensation system with a higher T_c . To ensure effective recovery of RCb and limonene from waste tyres, the hot tarry volatiles require rapid removal from the kiln and effective condensation in the oil trap to avoid cracking or recondensation on the RCb.

4.2. Effect of pyrolysis conditions on RCb characteristics

Surface area and surface activity are important determinants of RCb quality. These characteristics can be compromised by three types of contaminants: inorganics; volatile matter; and carbonaceous residues (see Table 5). Inorganics include steel and zinc based compounds, but mainly derive from the ever-increasing use of silica-based fillers within the rubber matrix of automotive tyres (Stanculescu and Ikura, 2006). These components constituted $17.0 \pm 0.7\%$ of the VM-free char (see Section 3.3). Although silica-based fillers reduce requirement for fossil-fuel derived Cb, silica compromises the RCb quality. Recent research has shown that RCb ash content can be reduced from $20 \pm 30\%$ to $13 \pm 1\%$ by feedstock mixing and by selectively removing up to 40% of high-silica

Table 5
Contaminants which affect the performance of RCb and minimisation strategy.

Contaminant	Sub-categorisation	Causes	Minimisation strategy
Inorganics	SiO ₂ compounds	Tyre composition	Feedstock selectivity
	S compounds	Poor mixing	Demineralisation
	Metals	Ingrained particles in tyre tread	Use of pyrogenic organic fillers instead of SiO ₂
Volatile matter	Remaining bonded volatiles (Re-VM)	Low HHT	High HHT
		Low gas flows	High gas flow
	Recondensed volatiles (Rc-VM)	Poor mixing	More mixing
Carbonaceous residues	Char derived (C-CR)	Excessive HHT	Low HHT
	Syngas derived (S-CR)	High t-res	High gas circulation
		Low gas circulation	Minimise char abrasion

tyres (Bowles and Fowler, 2022). Post-production inorganic removal from RCb is more challenging. Hydrothermal or acid-base demineralisation techniques must be used (Chaala et al., 1996; Chan et al., 2011; Martínez et al., 2019), however this process is energy intensive, and the exhausted demineralisation medium is hazardous to dispose of and expensive to recover. The substitution of traditional carbon black and silica-based fillers for biogenic carbonaceous materials, e.g., pyrolysed coconut shells (Fan and Fowler, 2018), may synergistically reduce reliance on fossil-fuel derived fillers whilst also reducing inorganic contamination of RCb after pyrolysis.

Solid mass loss in the pyrolysis kiln is attributable to two processes: volatilisation, and gasification. RCb volatile matter can be sub-categorised into residual VM from the original rubber structure (Re-VM) and recondensed volatiles from the syngas (Rc-VM). Data from this study and others show that high pyrolysis HHTs produce RCb associated with low levels of Re-VM (Martínez et al., 2013; Williams et al., 1990), whereas low gas flows produced RCb with high levels of Rc-VM, even at higher HHT values. This supports previous evidence that mixing and gas-solid contact area are increasingly important when pyrolysing waste tyre rubber at lower temperatures (Bowles and Fowler, 2022). Alternatively, the application of a negative pressure by using a vacuum may also assist in the rapid removal of VM from RCb (Foong et al., 2020). In RCb-650 °C, ash content increases (18.4% vs 17.0% for RCb-550 °C) yet yields do not decrease by a similar proportion ($36.6 \pm 0.3\%$ vs $36.0 \pm 0.2\%$). Assuming that all ash remains in the char fraction during pyrolysis, this suggests that a limited degree of RCb carbon degradation occurs between RCb-550 °C and RCb-650 °C (San Miguel et al., 2003).

A small proportion of the volatilised hydrocarbons may undergo cyclic recombination reactions thereby forming polyaromatic hydrocarbons (PAHs) that re-enter the solid phase and bond to the surface of the carbon black, forming soot-like carbonaceous residue (Cataldo, 2020; Martinez et al., 2021). Suggested mechanisms regarding the formation of these compounds are provided in Fig. 7. These PAHs contaminate oxygen-containing functional groups on the surface of the carbon black compounds, which are primarily carboxylic, quinonic, phenolic, or lactonic (Stanculescu and Ikura, 2006). PAH deposition over these groups greatly reduces the bonding capacity of RCb with viscous polymer matrices in recycled products. The toluene extraction results, which are lower for the RCbs measured here when compared to the virgin carbon black alternatives, suggest that toluene extractable PAHs form during pyrolysis and contaminate the surface of the RCb. The slight reduction in the transmissibility of toluene extract for RCb-650 °C ($93.2 \pm 0.2\%$) as opposed to RCb-550 °C ($94.8 \pm 0.8\%$) suggests these compounds may form at higher temperatures, or higher residence times over a certain HHT. The batch-operation of this pyrolysis kiln, combined with a low heating rate, meant that cooling times were high, potentially promoting the formation of these residues. Further experiments investigating carbonaceous residue formation at higher heating rates are recommended.

Previous studies have suggested that the presence of carbonaceous residues (CR) is the dominant limiting factor affecting the performance of RCb in recycled polymers and rubbers (Cardona-Urbe et al., 2021). Carbon black only consists of 1% PAHs, which cover approximately 8.7% of the surface N660 grade carbon black, as shown by XPS C1–C5 peaks (Martinez et al., 2021). In

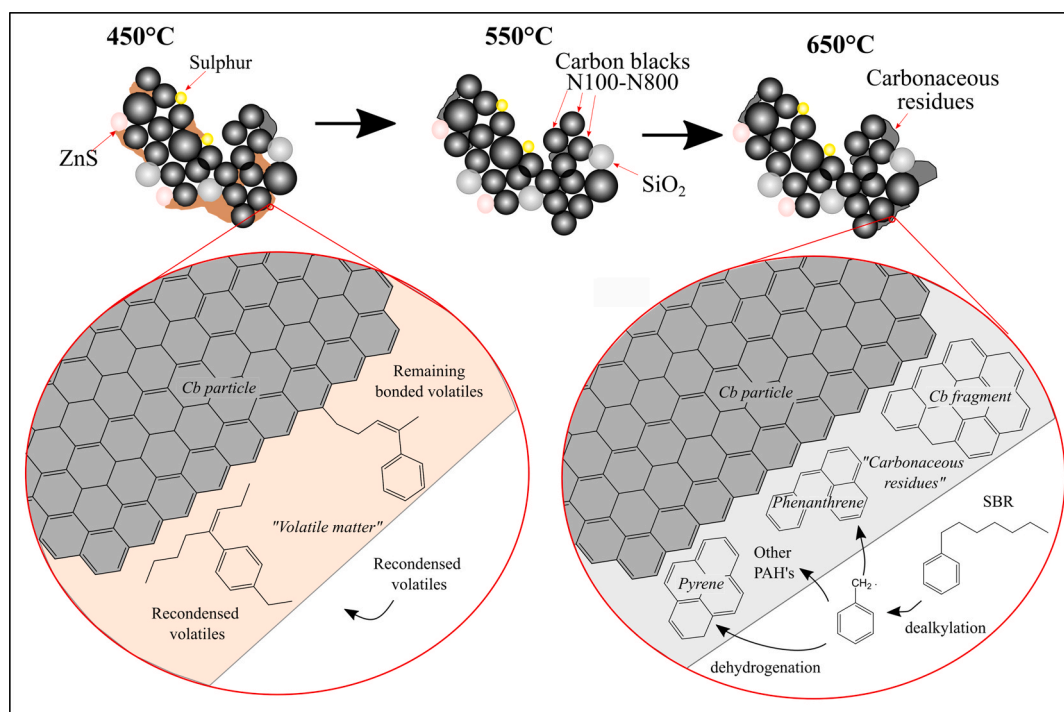


Fig. 7. Evolution of a recovered carbon black (RCb) aggregate as a function of pyrolysis highest heating temperature (HHT). Detailed schematics of possible molecular interactions are shown (Cataldo, 2020; Pantea et al., 2003; Yu et al., 2020).

comparison, 45.4% of RCbs surface (Roy et al., 1995, 1997; Zhang et al., 2008) was found to be covered by approximately 17% carbonaceous residues, as determined by SEM-EDC, FTIR and Raman spectroscopy (Cataldo, 2020). This is why in-rubber analyses have shown that RCbs have dispersion and bonding characteristics which are more similar to N774 grade carbon black (Norris et al., 2014), despite showing colloidal properties similar to N330 (as is the case here). Further chemical characterisation is required for RCb-CR with respect to coverage, and electronic environment. GC-MS has been used on RCb ethanolic extract to identify alkylated monocyclic aromatics, alkylated naphthalenes, and larger PAHs (Cataldo, 2020). Larger PAHs may also have been present which were not dissolved by the ethanol solvent. Analysis of the RCb extract using a stronger solvent (such as dichloromethane or toluene) may facilitate quantification of these compounds and how their composition varies as a function of pyrolysis conditions. The effect of tyre pyrolysis on CR coverage, using these techniques, requires further investigation (Pantea et al., 2003).

4.3. Limonene formation during tyre pyrolysis

Limonene is formed during tyre pyrolysis through the depolymerisation of polyisoprene, via allylic radicals formed by the β -scission of the single carbon-carbon bonds during heat treatment (Williams and Taylor, 1994). Two competitive reactions can occur: further scissions can generate the monomer isoprene, or rearrangement and intramolecular cyclisation can form limonene (see Fig. 8) (Januszewicz et al., 2020a). MS ion peaks have shown higher activation energies for the limonene reaction, which according to the Arrhenius Equation, requires higher HHTs. Published reports suggest that HHT is the most important determinant of limonene production (Mkhize et al., 2016).

In this study, maximum limonene concentrations of 7.2 ± 0.4 wt% of TPO were measured at a HHT of 450°C , which is consistent with previous data reporting limonene contents of 7–8% at temperatures of around 450 – 500°C (Cunliffe and Williams, 1998; Mkhize et al., 2016; Mkhize et al., 2019; Rofiqul et al., 2007). High limonene yields have been reported in TPO derived from heavy truck tyres, which was attributed to higher NR contents, and in TPO produced from vacuum pyrolysis which allows for volatilisation at lower HHTs, with shorter volatile residence times, thereby reducing degradation (Pakdel et al., 2001; Roy et al., 1999). Limonene decomposition has been found to occur at temperatures of $>500^\circ\text{C}$, forming compounds such as trimethyl benzene, m-cymene and indane, via aromatisation or decomposition to isoprene via the diallyl radical (Danon et al., 2015; Januszewicz et al., 2020a; Mkhize et al., 2016). An alternative mechanism of limonene decomposition within the hot furnace via free radical homolytic fission is proposed in Fig. 8. At higher pyrolysis temperatures, TPO limonene recoverability decreased significantly (8.7 ± 2.0 g/kg of steel-free waste tyres for TPO- 650°C vs 17.4 ± 0.7 g/kg for TPO- 550°C), suggesting degradation, supporting previous evidence elucidated via TPO differential thermogravimetric curves (Mkhize et al., 2019).

Extraction of limonene from the TPO can be achieved via repeated distillation at 170 – 190°C (Stanculescu and Ikura, 2006; Williams and Brindle, 2003), preferably with packed distillation columns (Pakdel et al., 2001), or via ion chromatography or reactive distillation (Januszewicz et al., 2020b). However, the cost-effective separation and purification of tyre-derived limonene is currently the biggest limiting factor preventing it from being recovered from waste tyres at a commercial scale. Initial limonene enrichment can be achieved using a simple steam distillation apparatus, which was evaluated in this study, and increased the limonene concentration from 7.2% to 16.3% within the light naptha fraction thereby achieving similar limonene concentrations to the 170 – 190°C boiling point cut reported elsewhere (Januszewicz et al., 2020a). Redistillations have been shown to further increase limonene concentrations of the naptha fraction to 32–37% (Pakdel et al., 2001). Mesh-packed distillation columns, which provide a much higher mass transfer efficiency, a lower pressure drop, and thus a lower required column height, have been used to produce fractions of 50–92% limonene (Pakdel et al., 2001). Distillation mechanisms are particularly attractive for initial extraction of limonene, due to the high temperature of the syngas at the kiln point of exit ($\sim 500^\circ\text{C}$), enabling waste heat recycling to generate initial naptha fractions. These temperature selective condensations would be particularly applicable to continuous pyrolysis systems and should be the focus of future research.

5. Conclusions

- A systematic analysis of recovered carbon black, tyre pyrolysis oil, and limonene recoverability from waste automotive tyres using a batch, rotary pyrolysis kiln has been conducted.
- The RCb with the lowest VM content ($0.2 \pm 0.3\%$ VM) was produced from pyrolysing a low sample mass (100 g) at a HHT of 550°C with a high gas flow rate (2000 mL N_2/min). This RCb had a high surface area (77.7 ± 2 m²/g vs 42.4 ± 0.9 m²/g for N550 carbon black), a high transmissibility of toluene extract ($94.8 \pm 0.8\%$ vs $99.0 \pm 0.7\%$ for N550), but also a high ash content ($17.0 \pm 0.7\%$ vs $2.1 \pm 0.1\%$ for N550).
- A maximum oil yield of $38.4 \pm 0.9\%$ was achieved by pyrolysing a high sample mass (200 g) at a HHT of 550°C with a low gas flow rate (400 mL N_2/min). This oil contained 4.5 ± 0.1 wt% of limonene implying that 17.4 ± 0.7 g could be produced per kilogram of steel-free waste tyre feedstock.
- The ratio of pyrolysing material to gas flow becomes more important when pyrolysis is undertaken at lower temperatures. Low temperature pyrolysis is preferable to avoid limonene cracking to less valuable products, and to minimise carbonaceous residue deposition, which contaminates RCb.
- Future research objectives include a reduction of RCb ash and carbonaceous residue content, and the extraction of limonene from the TPO thereby improving the recovery of these recyclable products.
- Optimisation using a system with minimum volatile residence time within the kiln, effective mixing, and a larger more efficient oil trap is recommended to maximise the recovery of both limonene and RCb from the same reactor.
- The production of RCb and limonene, alongside the remaining tyre pyrolysis oil, gas, and steel would significantly valorise this currently problematic waste stream, thereby incentivising recycling and promoting a more circular tyre lifecycle.

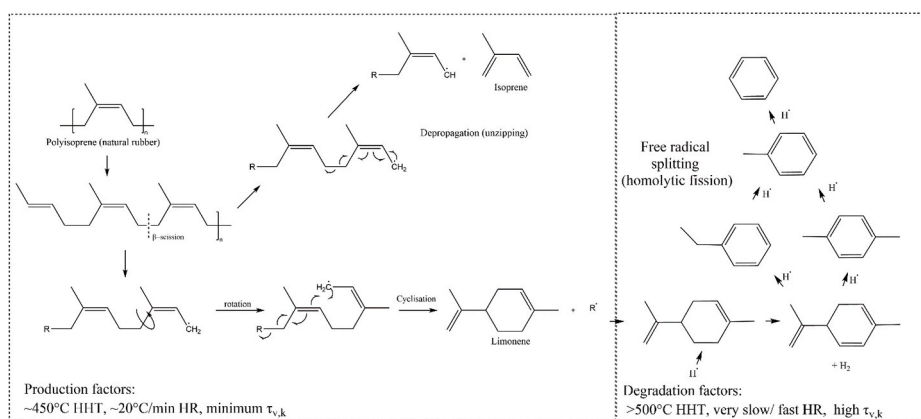


Fig. 8. Suggested mechanisms of the formation of limonene from natural rubber during tyre pyrolysis and subsequent degradation (Danon et al., 2015; Mkhize et al., 2016).

CRediT author statement

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Geoffrey D Fowler: Supervision, Writing - Review & Editing, Methodology.

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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.

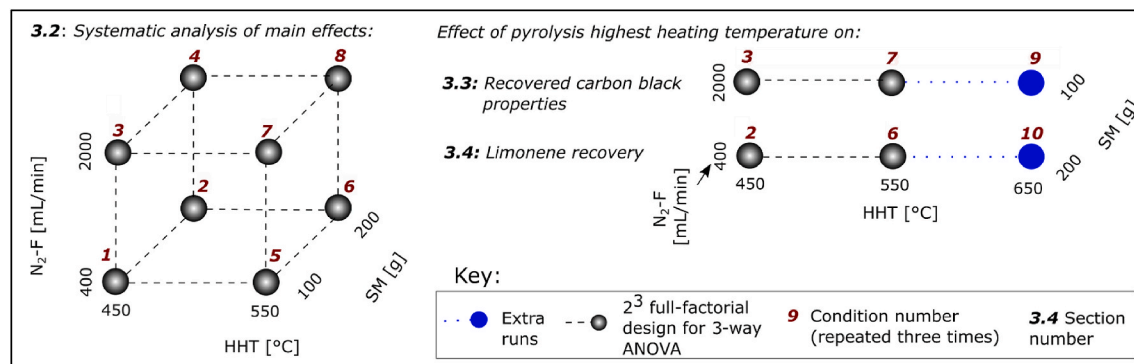
Data availability

Data will be made available on request.

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Appendix A. Experimental design deployed in this study



Appendix B. Showing the results of this study. HHT = Highest Heating Temperature. N₂-F: nitrogen gas flowrate, SM: sample mass pyrolysed, RCB-Y: char (RCB) yield, O-Y: Oil yield, G-Y: gas yield,. * = determined by difference

Condition	HHT [°C]	N ₂ -F [mL/min]	SM [g]	RCB-Y [%]	O-Y [%]	G-Y* [%]	RCB-VM [%]
1	450	400	100	51.5 ± 1.0	17.4 ± 0.6	31.2 ± 1.0	29.3 ± 1.6
2	450	400	200	51.4 ± 2.8	21.5 ± 1.5	27.1 ± 1.7	37.4 ± 4.0
3	450	2000	100	49.3 ± 0.5	16.5 ± 0.2	34.3 ± 0.3	25.5 ± 0.9
4	450	2000	200	51.8 ± 2.7	25.1 ± 0.5	23.0 ± 2.6	26.5 ± 3.8
5	550	400	100	38.7 ± 2.3	33.0 ± 1.5	28.3 ± 3.8	0.6 ± 0.7
6	550	400	200	37.2 ± 0.2	38.4 ± 0.9	24.4 ± 0.9	4.2 ± 1.1
7	550	2000	100	36.5 ± 0.2	26.1 ± 2.1	37.4 ± 1.9	0.2 ± 0.3
8	550	2000	200	37.1 ± 1.0	34.3 ± 0.6	28.6 ± 1.6	2.1 ± 1.5
9	650	2000	100	36.2 ± 0.3	26.6 ± 1.1	37.2 ± 1.0	0.0 ± <0.1
10	650	400	200	36.0 ± 0.4	37.9 ± 0.8	18.5 ± 1.9	2.1 ± 3.0

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