

# The effect of pre-pyrolysis chemical treatment of waste tyre rubber crumbs: comparison between pre-treated and conventional waste tyre-derived oil

Phuti Cedrick Tsipa,<sup>a,b\*</sup> Mapoloko Mpho Phiri,<sup>a</sup> Samuel Ayodele Iwarere,<sup>c\*</sup> Ntandoyenkosi Malusi Mkhize,<sup>b</sup> Mohau Justice Phiri<sup>a</sup> and Shanganyane Percy Hlangothi<sup>a</sup>



## Abstract

**BACKGROUND:** Pyrolysis process is one of the most effective recycling methods due to its ability to recover products like gas, oil and char with oil being the major/important product. The shortcomings of waste tyre-derived oil from the conventional pyrolysis process are that the oil contains high amounts of sulfur and polycyclic aromatic hydrocarbons (PAHs) and has a pungent smell, which makes it difficult to utilize further. The aim of this study is to investigate the effect of chemical pre-treated waste tyre rubber crumb-derived oil *versus* conventional waste tyre oil. The instrumentation utilized in this study was to solely investigate the shortcomings of waste tyre pyrolysis (high sulfur and PAH content and also high temperature required for waste tyre pyrolysis).

**RESULTS:** The results showed a reduction in amounts of both sulfur and PAHs in treated waste tyre-derived oil by about 83% and 77% respectively. Also, there was a reduction in initial pyrolysis temperature for the treated waste tyre crumb as compared to untreated waste tyre crumb: a temperature range of 96–115 °C for treated waste tyre crumbs as compared to 300–400 °C for untreated waste tyre crumbs.

**CONCLUSIONS:** The success of this study means the production of quality oil at a low temperature with lower amounts of PAHs and sulfur and less odour, plus the possibilities of it being used as a petroleum fuel or for extraction of important compounds like benzene, toluene, xylene, limonene and C<sub>12</sub>–C<sub>20</sub> acids.

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Supporting information may be found in the online version of this article.

**Keywords:** pyrolysis; chemical pre-treatment; waste tyre rubber crumb; sulfur; polycyclic aromatic hydrocarbon

## INTRODUCTION

The global growth of the automotive industry has caused an increase in the production of tyres. This in turn has resulted in an unavoidable steady increase in waste tyres or end-of-life tyres. It is estimated that about 60–100 million tonnes of waste tyres are abandoned in South Africa alone while approximately 11 million tonnes are added each year.<sup>1</sup> The complex nature of tyres makes it difficult for them to undergo biological degradation, hence an increase in stockpiles in landfills.<sup>2–4</sup> This raises a global ecological/environmental concern due to the threat these waste tyres pose in landfills.<sup>5–7</sup> This has prompted researchers all over the world to pursue innovative ways to recycle waste tyres. Pyrolysis is regarded as one of the most efficient recycling methods for waste tyres.<sup>8,9</sup> The process involves thermal decomposition of tyres in the absence of oxygen, to obtain their organic and inorganic components in the form of gases, oil and char.<sup>10,11</sup> The most attractive product is the

\* Correspondence to: PC Tsipa, Department of Chemistry, Nelson Mandela University, Centre for Rubber Science & Technology, PO Box 77000, Port Elizabeth, 6301, South Africa, E-mail: [s215375548@mandela.ac.za](mailto:s215375548@mandela.ac.za); or SA Iwarere, Department of Chemical Engineering, Faculty of Engineering, Built Environment, and Information Technology, University of Pretoria, Lynnwood Road, Hatfield, Pretoria, 0028, South Africa. E-mail: [samuel.iwarere@up.ac.za](mailto:samuel.iwarere@up.ac.za)

a Department of Chemistry, Nelson Mandela University, Centre for Rubber Science & Technology, Port Elizabeth, South Africa

b Chemical Engineering Discipline, University of KwaZulu-Natal, Glenwood, South Africa

c Department of Chemical Engineering, Faculty of Engineering, Built Environment, and Information Technology, University of Pretoria, Pretoria, South Africa

liquid product (waste tyre-derived oil, TDO) because of its many possible uses which include production of fuel, industrial solvents, resins, adhesives and dispersion agents for pigmentation.<sup>12–15</sup>

The disadvantages of this oil are that the flash point is very low compared to commercial petroleum fuels, and it has high levels of carbon residue posing a threat of depositing on an engine if combusted.<sup>16</sup> This is because the unrefined pyrolytic oil contains a mixture of compounds, resulting in a wide distillation range. Furthermore, pyrolytic oil contains high content of sulfur and polycyclic aromatic hydrocarbons (PAHs), which makes it difficult for it to be used as fuel.<sup>17</sup> TDO in the literature is recorded as typically having a high sulfur content of about 1.0–1.4 wt%, which is caused by the vulcanizing agents used in the tyre formulation.<sup>18</sup> Sulfur compounds present in TDO such as thiols, thiophenes, benzothiophenes and dibenzothiophenes have undesirable properties especially when combusted, which include being corrosive and causing irritation and respiratory diseases.<sup>19,20</sup>

Ngxangxa<sup>21</sup> studied the effect of temperature on the formation of compounds in TDO and the author's findings showed that D,L-limonene was one of the major constituents in TDOs. This was also reported by several other authors who conducted related studies.<sup>22,23</sup> In principle, it was found that when pyrolysis of waste tyre rubber crumbs is conducted at temperatures below 500 °C limonene undergoes isomerization forming cyclohexene isomers. At 500–600 °C aromatization occurs from terpenes (limonene) to form xylene and toluene via intramolecular hydrogen transformation, followed by the loss of ethane. Trimethylbenzene is formed through a similar path, although it only occurs later at slightly higher temperature. At 700 °C, aromatization occurs forming aromatic compounds and as the temperature increases, PAHs form.<sup>21,24</sup>

There have been some developments in trying to mitigate some of the temperature-related challenges in waste tyre pyrolysis. These include the use of catalysts (a specific component added to a system to improve chemical reaction specificity), co-pyrolysis (a process that involves two or more materials as feedstock to be pyrolysed) and desulfurization of TDO (which can be described as chemical assistance to catalysts to reduce sulfur content in the tyre-derived oil).

Duan *et al.*<sup>25</sup> studied the co-pyrolysis of microalgae and waste tyres in supercritical ethanol. Results obtained from that study showed a decrease in required temperature, deoxygenation, denitrogenation, desulfurization and the bio-oil produced possessed an energy density close to that of petroleum diesels. Shah *et al.*<sup>26</sup> investigated the co-pyrolysis of cotton stalks and waste tyres. The focus of the study was on the quantity and quality of the oil. The results reported showed a 10% increase in the liquid product of 2:3 cotton stalk to waste tyre ratio. Furthermore, the oil produced from this ratio of materials achieved a calorific value of 41 MJ mol<sup>-1</sup>, which is comparable to that of commercial diesel. Martínez *et al.*<sup>27</sup> studied the benefits of co-pyrolysing pine woodchips with waste tyre rubber crumb, seeming to stabilize the bio-oil. They observed that radical interactions from woodchips and waste tyre rubber crumb co-pyrolysis promoted the formation of a stable bio-oil with upgraded properties. A 90:10 blend showed better result in improving properties like reduced sulfur content, water content and increasing bio-oil viscosity. Several researchers such as Zhang *et al.*<sup>28</sup> and Singh *et al.*<sup>29</sup> highlighted the key reason behind co-pyrolysis, which is the positive interaction between the two or more feedstocks to improve the quality and quantity of the oil.

The use of catalysts in the pyrolysis process not only enhances the reaction kinetics by cracking high-molecular-weight compounds into lighter compounds, but also lowers the activation energy of the pyrolysis system.<sup>30</sup> Several studies have been done on the use of catalysts in tyre pyrolysis as it was a breakthrough.<sup>31–33</sup> The TDO produced when using catalysts showed improvements in physical properties and resembled those of commercial diesel. Osayi and Osifo<sup>34</sup> conducted a study comparing the physical properties of uncatalysed and catalysed (zeolite NaY catalyst) TDO and commercial diesel. The reported results showed that some of the properties were not affected such as density, viscosity, flash point and pour point and some properties were improved in the catalysed oil such as refractive index, heating value and sulfur content. Hydro-desulfurization catalysed by molybdenum (Mo), nickel–Mo or cobalt–Mo supported on alumina was used by Jantarksa *et al.*<sup>35</sup> for desulfurization of TDO. The maximum sulfur removal (87.8%) was achieved for TDO. The pyrolysis process of waste tyre is still under development. The recently developed technology concerning pyrolysis of waste tyres is the microwave pyrolysis reactor. This reactor enhances the distribution of heat transfer into the feedstock (homogeneous heat distribution) and permits operation under isothermal conditions. Bett *et al.*<sup>36</sup> used a microwave reactor to investigate the optimization of TDO. The parameters used in the study were reactor power, reaction time and particle size of the feedstock. With the optimum conditions used, those authors were able to produce about 39% liquid product with physicochemical properties similar to those of commercial diesel.

The aim of the study reported here was to find an alternative method to assist waste tyre rubber crumb pyrolysis in minimizing some of the thorny issues typically associated with the process. These include high operating temperatures, high content of sulfur and/or sulfur-containing compounds and high PAH content. The adopted approach involved chemical pre-treatment of waste tyre rubber crumbs before pyrolysis. This approach was informed by the scientific knowledge that organic solvents swell a polymer easily under ambient temperature causing the polymer matrix to open up, giving access for an acid to break carbon–carbon and/or carbon–sulfur bonds in the polymer chains. The hypothesis was that the pre-pyrolysis treatment stage can cause waste tyres to be pyrolysable at lower temperatures and in the process also reduce the content of sulfur and/or sulfur-containing compounds by breaking the vulcanization-induced sulfur–sulfur bonds, and thereby improve the quality or properties of the resultant oil fraction.

In the study reported here, the effect of the chemical pre-treatment and of low temperature on the quality of the TDO produced was studied. The quality of TDO collected in the absence of chemical pre-treatment was compared to that of the TDO collected from the pyrolysis of chemically pre-treated waste tyre rubber crumbs. Thus, the chemical composition (in terms of PAHs) and sulfur content of the TDO from both processes were investigated. Gas chromatography–mass spectrometry (GC–MS) and Fourier transform infrared (FTIR) spectroscopy were used to investigate the chemical composition of the TDO; and GC coupled with a flame photometer detector (GC–FPD) was employed to estimate the sulfur and/or sulfur-containing compounds present in the oil. This study is a sequel to a previous one conducted in our laboratories where the effect of chemical pre-treatment of waste tyre rubber crumbs on the pyrolysis temperature was investigated.<sup>37</sup> In that earlier study, it was shown that the chemical mixture was selected based on its ability to rupture the polymer backbone, toxicity, semi-

recyclability and cost. Liquid product is an important part of the waste tyre pyrolysis process and therefore the success of this study may result in an industrially acceptable quality oil.

## EXPERIMENTAL

### Materials

Waste tyre rubber crumbs with 30 mesh particle size used in this study were purchased from MATHE Group (PTY) Ltd, South Africa. The chemical mixture used consisted of protonic acid (69% purity supplied by Merck) and organic solvent (laboratory grade: supplied by Merck).

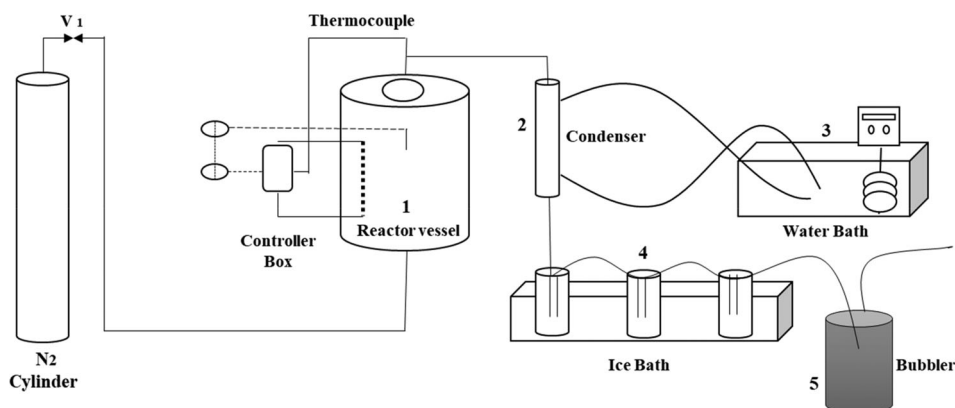
### Methods

#### Chemical pre-treatment

Chemical mixture was prepared by mixing protonic acid and organic solvent mixed at a ratio of 5:95, resulting in a two-phase heterogeneous mixture. Waste tyre rubber crumbs were soaked in this chemical mixture and stirred at 350 rpm for 2–3 h under ambient conditions. The liquid and solids were separated and washed with water to terminate and neutralize the reaction. The aqueous layer was separated from the organic layer, and the excess solvent evaporated using a rotary evaporator, and recovered. Approximately 44.4% of the solvent was recovered with a standard deviation of  $\pm 0.67$  for at least three experiments due to the solvent system's volatility. The three R method (repeatability, reproducibility and recovery) was used to validate this method. This was done to measure the precision or the closeness from a series of replicated experiments and reflect the random errors which occur in this method. The solid was dried in a fume hood/by air for 24 h and transferred to a desiccator to ensure that it was properly dried (see supporting information, Fig. S1). The dried treated solid was then subjected to pyrolysis.

#### Reactor

A vertical fixed-bed pyrolysis reactor with a 40 g capacity was used. The reactor consisted of three main parts: first – reactor vessel which consisted of two parts, heating jacket and reactor cylinder; second – condenser which was connected to a water bath to regulate the condenser temperature; and lastly – collector, which was subjected to different temperatures for oil fractionation/separation (Scheme 1).



**Scheme 1.** Pyrolysis reactor.

#### Pyrolysis conditions optimization

Controlled variable method was used for pyrolysis parameters/conditions optimization. This method follows the principle of observing the dependency of individual variables, all other variables being kept constant (controlled variables) so that the effect of one variable could be tested (independent variable).<sup>38</sup> Temperature was the first condition to be optimized then nitrogen flow rate and collector temperature. Two conditions were kept constant at a time to see the effect of each condition on the product yields. Table 1 presents the pyrolysis condition optimization in terms of product yields. A temperature of 280 °C was chosen as optimum for the treatment of tyre crumbs due to the objective of this study (reducing the temperature) and maximum yield of liquid product was achieved at this temperature. The other conditions (gas flow rate and collector temperature) were optimized based on this temperature. It was found that a decrease in the nitrogen volumetric flow leads to an increase in liquid product yield and a decrease in gas product; this is postulated to be due to the increased residence time of the pyrolytic vapour in the system. At lower volumetric flow rate, under 3 L min<sup>-1</sup>, the pyrolytic vapour condenses inside the system, which resulted in the blockage of the system. Dry ice was used to capture the lower molecular weight compounds, but it was not used for the first and second collectors to avoid blocking the lines. For untreated waste tyre rubber crumbs, 600 °C was deliberately chosen as a suitable processing temperature because at this temperature all volatile/decomposable materials in the tyre crumbs are usually pyrolysed. Flow rate and collector temperature conditions used were the same as the optimized ones used for treated tyre crumbs.

#### Characterization

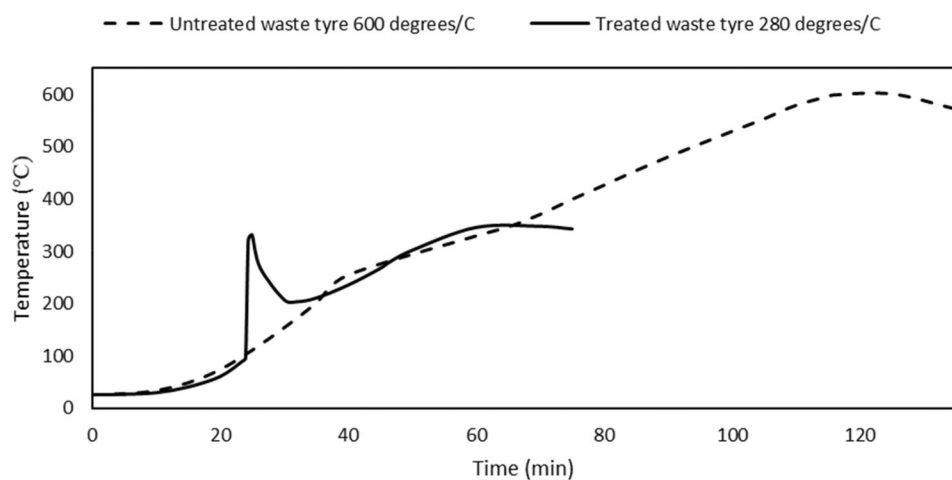
The following instrumentation was used to analyse products obtained from the 40 g capacity vertical fixed-bed pyrolysis reactor.

#### Solid samples

Bruker attenuated reflected (ATR) single reflection diamond crystal, FTIR-Bruker Tensor 27, spectral range 400–4000 cm<sup>-1</sup>. CHNS analysis: Thermo Scientific Flash 2000 coupled to an LC premier micro-mass spectrometer. Scanning electron microscopy (SEM): JSM-IT 100 equipped with JEOL SEM technologies with backscattered electron composition detector. Differential thermal analysis (DTA): Shimadzu DTG-60AH simultaneous DTA-TG; and SDT: TA simultaneous DSC-TGA (SDT) Q600.

**Table 1.** Pyrolysis optimization

| Temperature optimization | Nitrogen volumetric flow rate at 280 °C |              |           |          |                                  |              |             | Collector temperature                    | Char (%)     | Oil (%)   | Gas (%)     |
|--------------------------|---|--------------|-----------|----------|----------------------------------|--------------|-------------|--|--------------|-----------|-------------|
|                          | Temperature (°C)                        | Char (%)     | Oil (%)   | Gas (%)  | Flow rate (L min <sup>-1</sup> ) | Char (%)     | Oil (%)     |  |              |           |             |
| 200                      | 55                                      | 23.1         | 21.9      | 6        | 48.75                            | 27.25        | 24          | C1, C2 and C3 – Ice                      | 50           | 40.25     | 9.75        |
| 250                      | 54.1                                    | 24.3         | 21.6      | 5        | 49                               | 36.5         | 14.5        | <b>C1 and C2 – ice; and C3 – dry ice</b> | <b>50.25</b> | <b>46</b> | <b>3.75</b> |
| 270                      | 49.2                                    | 25           | 25.8      | <b>3</b> | <b>50</b>                        | <b>40.25</b> | <b>9.75</b> |  |              |           |             |
| <b>280</b>               | <b>48.75</b>                            | <b>27.25</b> | <b>24</b> | 2        | —                                | —            | —           |  |              |           |             |



**Figure 1.** Pyrolysis temperature–time profile. Summary of temperature history over time to monitor the temperature activity in the reactor.

### Liquid samples

For FTIR, the same specifications as for solid samples were used. Shimadzu GC–MS column: SH-Rxi-5 MS (30 m, 0.25 mm, 0.25 μm); and Shimadzu GC–FPD column: Zeblon ZB-1 (30 m, 0.25 mm, 0.25 μm).

## RESULTS AND DISCUSSION

### Solids characterization

#### Pyrolysis process

A fixed-bed vertical pyrolysis reactor was used with a 40 g feedstock capacity. The following conditions were used: gas flow rate, 20 mL min<sup>-1</sup>; gas volumetric flow rate, 3 L min<sup>-1</sup>; collector temperature, C1 and C2, ice (around 3–5 °C) and C3, dry ice (approximately –78.7 °C). Waste tyres contain at least 50% of rubber composition that could be pyrolysed, due to the pyrolysis reactor's ability to reach higher temperatures in the absence of oxygen.<sup>39,40</sup> Larger parts of the pyrolysable substances are from the decomposition of two rubbers, natural rubber (NR) and styrene–butadiene rubber (SBR). NR decomposes at a temperature range of 300–350 °C and SBR decomposes at a temperature range of 350–450 °C.<sup>40</sup>

#### Pyrolysis temperature–time programme

A comparison of temperature–time profile between treated and untreated waste tyre samples is shown in Fig. 1. The untreated tyre sample follows pyrolysis temperature programme with a slight temperature increase around 240–250 °C. In our previous

study,<sup>37</sup> this phenomenon was attributed to the presence and decomposition energy of the processing oil typically added in tyre formulations. The treated tyre sample graph spiked in the region between 96 and 333 °C. This follows a phenomenon known as self-pyrolysis, which is described to result from chain reaction heat-up causing coupling among oil, oxidation, heat transfer and gas.<sup>41,42</sup> This event's duration was under 7 min, during which the liquid product rapidly flushed out of the condenser into the collector. Furthermore, it was also observed that light molecular weight liquid fraction condensed first, followed by the heavier liquid fraction which dripped slowly into the collector, taking over an hour to complete.

Duan *et al.*<sup>25</sup> also observed a decrease in temperature (from 500 to 330 °C) while investigating the co-pyrolysis of waste tyre and microalgae in supercritical ethanol. The suggested conclusion was that ethanol, acidic characters and zinc oxide (ZnO) were instrumental in lowering the temperature. Firstly, those authors suggested that microalgae would decompose first at lower temperature to produce intermediate compounds that will affect the stability of the molecular chains and promote the conversion of the rubber in supercritical ethanol.<sup>25,43</sup> Acidic characters also play an important role in the conversion of waste tyres, the principle following the mechanism of acidic catalysis mentioned in several studies.<sup>25,44</sup> Lastly, tyres contain ZnO, which was reported to help break down polymers into shorter chains.

The results obtained from the experiments conducted are summarized in Table 2 and are categorized based on the amount of



solid, liquid and gas recovered, and the time it took for the process to end. The weight percentage of the products was calculated using mass balance. The products recovered from untreated and treated tyre crumb pyrolysis were compared by the time taken for the process to complete, product yields, fractions of oil produced, colour of the oil and odour. The pyrolysis process of the untreated sample started at about 60 min, when smoke cloudiness was observed in the collector, and overall time taken for the process to complete was 116 min. Product yields were recorded as follows: about 7% gas, 55% liquid (attributed to three fractions of liquid: light, light to medium and heavy fractions) and 38% char. For the pre-treated sample, pyrolysis started at about 24 min and overall time taken for the process to complete was about 46 min. The yields of the different products were 50% solid product, 46% liquid and 4% gas. The liquid fractions produced were collected in three separate collectors. It was interesting to observe that at a temperature range of 96–109 °C (event of sudden temperature spike), about 77% of the oil produced was a light fraction oil which was produced in 7 min. This light fraction oil had a fuel-like odour and appeared reddish in colour, the light-medium fraction also had fuel-like odour and appeared dark brown, while the heavier fraction oil had an unpleasant stench and appeared black in colour. The oils produced from pyrolysing untreated (A) and treated waste tyres (B) and their colours are shown in Fig. 2.

#### Spectroscopic analysis

**SEM analysis.** The morphology of untreated and treated tyre samples before pyrolysis was explored using SEM. Figure 3 shows SEM images of these samples at  $\times 50$  and  $\times 1000$  magnifications. It was

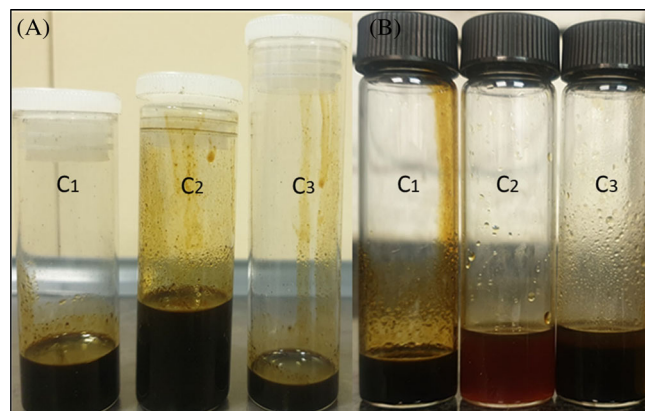
observed that after chemical treatment, the tyre crumb matrix developed pores, which were suspected of assisting the pyrolysis process and enabled the process to take place at lower temperatures.<sup>45</sup> It has been reported that such pores in the sample matrix causes ease of heat diffusion and uniform heat flux, which leads to self-pyrolysis taking place.<sup>46,47</sup>

**FTIR spectroscopy of solid tyre rubber crumbs.** Treated and untreated waste tyre rubber crumb solid samples were analysed using ATR-FTIR. From the scans of untreated waste tyre rubber crumb before pyrolysis, NR- and SBR-related functional groups were identified: 1372–1450  $\text{cm}^{-1}$  is assigned to C–H bending of  $-\text{CH}_2$  and  $-\text{CH}_3$  in NR, 1600  $\text{cm}^{-1}$  is assigned to C=C in both 1,4-*cis*-isoprene (NR)<sup>48,49</sup> and butadiene (SBR) and lastly 698–804  $\text{cm}^{-1}$  is assigned to monosubstituted benzene in SBR.<sup>49</sup> After 600 °C pyrolysis of untreated waste tyre rubber, these peaks did not appear in the spectrum, only the dominant presence of carbon or char in the samples. This is because most of the volatile material had already decomposed.

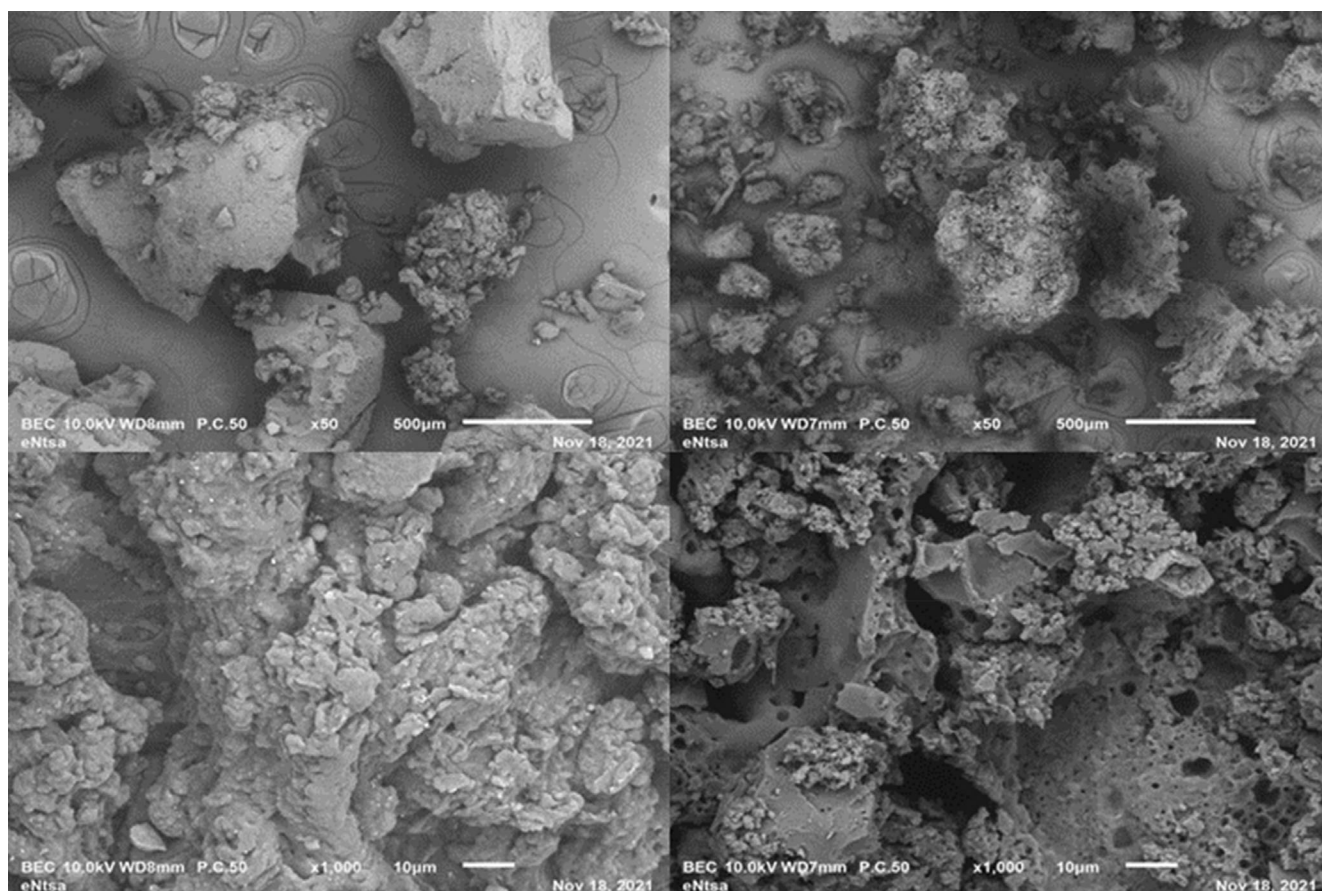
New functional group peaks were observed for the treated tyre crumb sample due to the chemical pre-treatment. A broad peak typical of O–H stretching was observed in the region between 3000 and 3400  $\text{cm}^{-1}$ ; another peak was observed at 1700  $\text{cm}^{-1}$ , which can be assigned to C=O.<sup>49</sup> It is clear that these functional groups formed during the treatment of tyre crumbs, which shows that oxidation took place in the sample. In addition, from 1500 to 804  $\text{cm}^{-1}$ , a broad peak typical of a combination of the following functional groups was observed: stretching of carbon atoms in the aromatic rings at 1493 and 1450  $\text{cm}^{-1}$ , styrene at 1074  $\text{cm}^{-1}$ , *cis*-polybutadiene unit at 1029  $\text{cm}^{-1}$  and =CH unit at 1400  $\text{cm}^{-1}$

**Table 2.** Summary of pyrolysis results of untreated and treated tyre crumb

|              | Treated crumb  |        |      | Untreated crumb                          |        |      | Lit. <sup>23</sup> (optimum temperature 475 °C) |        |     |
|--------------|--|--------|------|--|--------|------|---|--------|-----|
|              | Char   | Liquid | Gas  | Char                                     | Liquid | Gas  | Char  | Liquid | Gas |
| Amount (g)   | 20.1   | 18.4   | 1.5  | 15.3                                     | 21.82  | 2.89 | -   | -      | -   |
| Amount (wt%) | 50.25  | 46     | 3.75 | 38.25                                    | 54.54  | 7.21 | 37.3  | 58.2   | 4.5 |
| Oil odour    | C1 – mild tyre smell; C2 and C3 – petroleum-like smell |        |      | C1, C2 and C3 – pungent unpleasant smell |        |      | Pungent unpleasant tyre smell                   |        |     |
| Oil colour   | C1 – black; C2 – reddish; C3 – dark brown              |        |      | C1, C2 and C3 – black                    |        |      | Dark brown/black                                |        |     |
| Time         | 46:43 (min)  |        |      | 116 (min)                                |        |      | —   |        |     |



**Figure 2.** Pictorial image of oils produced from (A) untreated waste tyres and (B) treated waste tyre rubber crumbs.



**Figure 3.** SEM analysis: (A, C) untreated rubber crumb; (B, D) treated tyre crumbs; (A, B) at 500  $\mu\text{m}$ ,  $\times 50$  magnification and (C, D) at 10  $\mu\text{m}$ ,  $\times 1000$  magnification.

that occurs in butadiene unit.<sup>48,49</sup> It was hypothesized that these functional groups of the broad peak were caused by the distribution of chains due to chain scission during chemical treatment.

#### Thermal analysis – elemental (CHNS/O) and proximate analysis

The elemental composition and proximate analyses of untreated and treated tyre crumbs and results from literature are summarized in Table 3. It can be seen from the elemental analysis data that the carbon content of the treated tyre crumbs was less than that of untreated tyre crumb, the same being true for the literature. This was due to the chemical treatment which caused some carbon–carbon and carbon–sulfur chain breakage and therefore it could be possible that some carbons escaped in the form of small-molecule carbon-based gases. It was also observed that there was an increase in oxygen content in the treated samples. This observation was in line with FTIR results, which showed that the treated sample was oxidized.

It is well known that NR and SBR polymers decompose from 300 to 450  $^{\circ}\text{C}$ ; furthermore these two rubbers make up a major portion of a tyre crumb.<sup>40</sup> Proximate analysis results showed that about 19 wt% of moisture/low-molecular-weight compounds from the treated tyre crumb was expected to be pyrolysed, since the temperature used for the pyrolysis process was 280  $^{\circ}\text{C}$ . The proximate analysis results after pyrolysis of treated waste tyre are as follows: moisture, 3.92 wt%; volatiles/decomposables, 11.65 wt%; fixed carbon, 79.32 wt%; ash, 5.07 wt%. The results indicated that due to self-pyrolysis that took place, about 80%

of the decomposable/pyrolysable material was able to undergo pyrolysis. Only about 12% of the polymer in the treated tyre crumb was not pyrolysed. The polymer not pyrolysed was suggested to be SBR because it is known to decompose at 400–450  $^{\circ}\text{C}$ . Since the temperature in the reactor spiked to only 334  $^{\circ}\text{C}$ , this suggests that some of the SBR polymer chains were not broken during the treatment.

#### Liquid product characterization

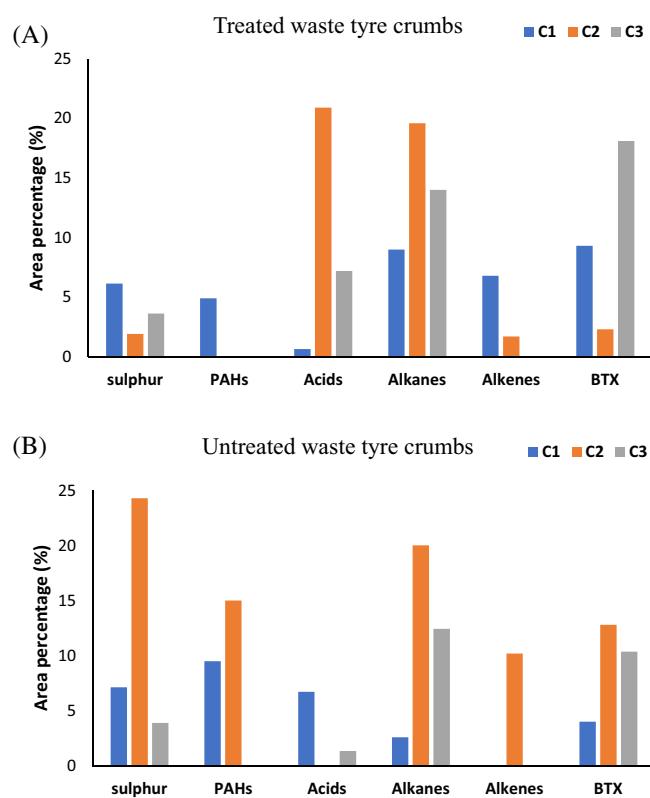
##### FTIR analysis

The following functional groups were assigned to the following peaks as seen in Fig. S2 in the supporting information: 3000–3400  $\text{cm}^{-1}$  is assigned to  $-\text{OH}$ , 2800–2900  $\text{cm}^{-1}$  to  $-\text{CH}$  stretch, 1700  $\text{cm}^{-1}$  to  $\text{C}=\text{O}$ , 1600  $\text{cm}^{-1}$  to  $\text{C}=\text{C}$ , 1374–1450  $\text{cm}^{-1}$  to  $-\text{CH}_2$  and  $\text{CH}_3$ , 1000–1260  $\text{cm}^{-1}$  to phenols and 804–900  $\text{cm}^{-1}$  to monosubstituted benzene. Treated waste tyre collector 2 (C2) exhibits  $-\text{OH}$  functional groups which can be seen at wavenumbers between 3400 and 3000  $\text{cm}^{-1}$  and phenol peak at 1000–1260  $\text{cm}^{-1}$ . This also shows that the oil is oxidized. Untreated waste tyre collector 1 (C1) shows an intense monosubstituted peak at 732  $\text{cm}^{-1}$ , which means a similar monosubstituted benzene compound was formed during pyrolysis. This agrees with the literature, as Ngxangxa<sup>21</sup> showed that monosubstituted aromatics are formed at 500–600  $^{\circ}\text{C}$  in the oil from *L,D*-limonene. All the oil samples possess similar functional groups with bands of different intensities, from which it can be concluded that

**Table 3.** Elemental composition and proximate analysis results obtained from untreated and treated waste tyre crumbs compared to literature

|                    | Sample 1 UWT crumbs | Sample 2 TWT crumbs | Literature                       |                                  |
|--------------------|---------------------|---------------------|----------------------------------|----------------------------------|
|                    |                     |                     | Duan <i>et al.</i> <sup>25</sup> | Wang <i>et al.</i> <sup>50</sup> |
| CHNS/O             |                     |                     |                                  |                                  |
| Carbon (wt%)       | 80.62               | 57.23               | 78                               | 81                               |
| Hydrogen (wt%)     | 7.46                | 4.72                | 6.87                             | 6.6                              |
| Nitrogen (wt%)     | 0.42                | 6.54                | 1.4                              | 1.7                              |
| Sulfur (wt%)       | 1.76                | 1.13                | 1.9                              | 1.37                             |
| Oxygen (wt%)       | 9.74                | 30.19               | 1.63                             | 9.8                              |
| Proximate analysis |                     |                     |                                  |                                  |
| Moisture (wt%)     | 2.29                | 18.46               | 0                                | 0.7                              |
| Volatile (wt%)     | 57.75               | 39.82               | 68.93                            | 62.5                             |
| Fixed carbon (wt%) | 35.98               | 40.56               | 24.59                            | 27.9                             |
| Ash (wt%)          | 3.98                | 1.17                | 9                                | 8.9                              |

Abbreviations: UWT, untreated waste tyre; TWT, treated waste tyre.

**Figure 4.** Classifications of GC-MS compounds from (A) untreated TDO and (B) treated TDO in their respective collectors.

similar oil type could be produced using less energy due to chemical treatment.

#### GC-MS analysis

The GC-MS method for TDO was developed by optimization of the temperature programme for better separation in the column. It was observed from the chromatograms that there was a reduction in compounds present in the treated TDO as compared to untreated TDO (supporting information, Fig. S3). In addition, the former product contains a great/significant number of single aromatic compounds (benzene, toluene and xylene (BTX)) and long-

chain acids (e.g. hexadecenoic acid, heptadecanoic acid, etc.). These compounds have a high market value. Treated TDO also contained more alkane compounds as compared to untreated TDO. It can be seen from the data in Fig. 4 that untreated TDO has more sulfur and PAH compounds. Also, this oil contains more alkene compounds as compared to treated TDO, with *D,L*-limonene being the major compound.

In most pyrolysis studies, it has been recorded that tyre pyrolytic oil contains PAHs. These compounds are problematic because they are hazardous to the environment and are carcinogenic to humans.<sup>51-53</sup> In addition, the pyrolytic oils used for fuel have a potential to cause damage to an engine because combustion of these oils tends to form particles/deposits as they possess a high threshold soot index (TSI).<sup>18,54</sup> The improvement of the quality of this type of oil is important seeing that it causes complications if used for fuel. As explained by Ngxangxa,<sup>21</sup> at around 500–600 °C, aromatization of terpenes takes place forming BTX compounds. Further aromatization took place in the untreated tyre-derived oil as different compositions of naphthalene (PAH) compound were much produced. It was observed that there are fewer PAHs in the treated tyre crumbs than in untreated tyre crumbs, confirming that PAH reduction objective was successful.

#### GC-FPD analysis

GC-FPD is one of the common methods used in sulfur and phosphorus analysis. A FPD consists of three most important parts: first, the flame which burns the sample from the GC column; second, the chemiluminescence detector region for absorbing and emitting the light; lastly, the filters to isolate the sulfur and phosphorus emitted radiation and remove the interference before sending it to a computer. The FPD operates as follows: sulfur compounds from the GC column are burnt in a hydrogen-rich flame to produce S<sub>2</sub> which emits radiation near 400 nm. This radiation is monitored by a photomultiplier tube (see supporting information, Fig. S4).

GC-FPD analysis for sulfur content in the TDO produced was conducted following the ASTM D5623 standard method. ASTM D5623 is a standard test method for determining/verifying the sulfur-containing compounds in light petroleum liquids using GC coupled to a selective sulfur detector. Figure 5 shows overlaid chromatogram of untreated TDO fractions (Fig. 5(A)) and treated TDO fractions (Fig. 5(B)). This analysis was used to identify and

compare the amount of sulfur present in these oils. It can be observed from Fig. 5(A) that untreated TDO has relatively higher quantity of sulfur compounds as compared to the treated TDO shown in Fig. 5(B). It is suggested that chemical pre-treatment of the waste tyre rubber crumb caused breakage of some of the sulfur–sulfur and sulfur–carbon bonds which affected the sulfur content in the oil (see supporting information, Table S1). One of the observations made during the pre-treatment of waste tyre rubber crumbs was a yellowish-brown gas emission, which we suspect to be sulfurous (see supporting information, Fig. S5). Some of the sulfur compounds were attributed to H<sub>2</sub>S and SO<sub>x</sub> gases that may have evaporated during the pyrolysis process.

Equation (1) was used to calculate TDO sulfur content:

$$[S]_t = \sum gA_i = gA_i = \frac{[S]_o}{[S]_t} = \frac{[A]_o}{[A]_t} \quad (1)$$

where [S]<sub>t</sub> is the total sulfur concentration and [S]<sub>o</sub> is the initial concentration of the whole sample. [A]<sub>t</sub> and [A]<sub>o</sub> are the areas under the peaks of all the sulfur compounds. Table 4 summarizes the results calculated from GC-FPD compared to the literature.

**Table 4.** Summary of data gathered from GC-FPD analysis of untreated and treated waste tyre oil compared to literature

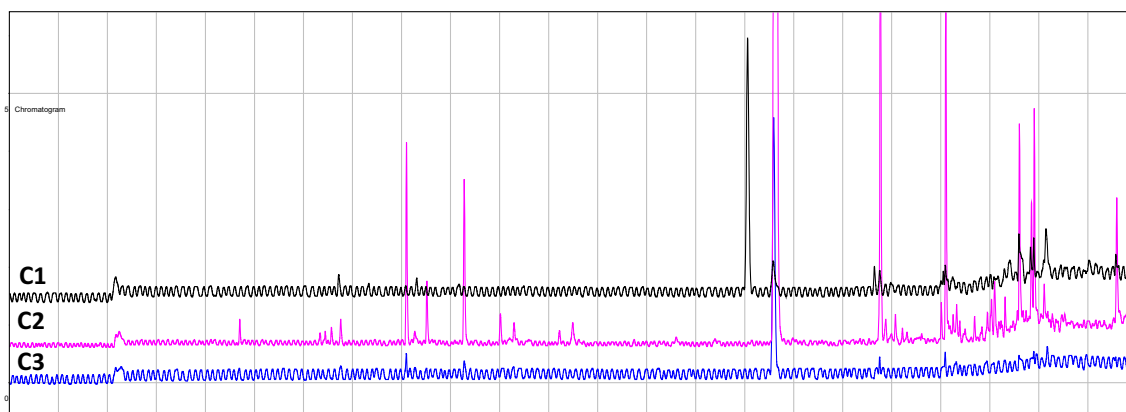
| Sulfur | Untreated TDO | Treated TDO | Literature TDO <sup>18</sup> |
|--------|---------------|-------------|------------------------------|
| ppm    | 6729          | 2223        | ca 7000–14 000               |
| wt%    | 0.67          | 0.22        | ca 0.7–1.40                  |

The total sulfur content in untreated TDO was 6729 ppm (0.67 wt%) and 2223 ppm (0.22 wt%) in treated TDO. The results obtained agree with those of several literature studies, where the range of sulfur content in TDO is 0.7–1.4 wt%.

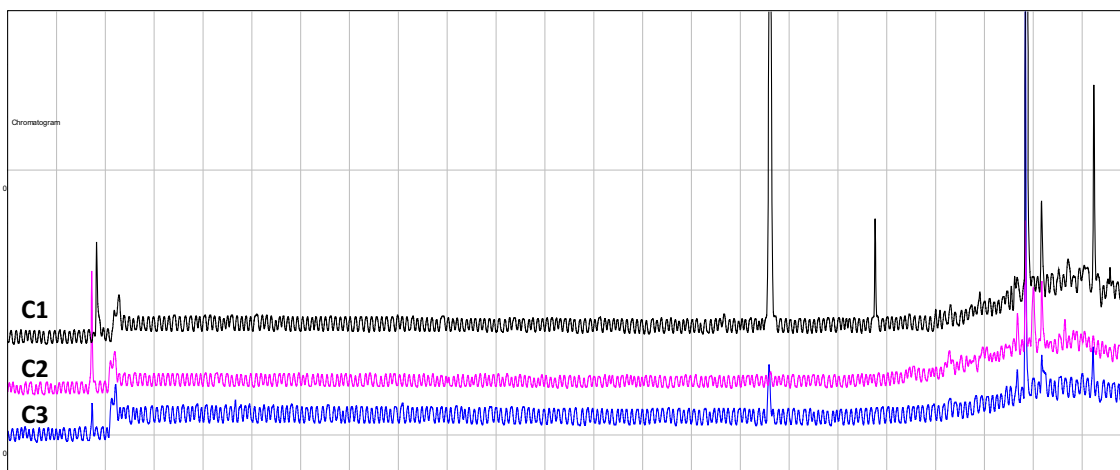
#### Mass balance

The purpose of mass balance is to trace the total mass distribution during pyrolysis. The method follows the principle that states that the starting mass should be equal to the mass of products; in this case the mass before pyrolysis is equal to the mass of products, which is the volatiles plus the char (mass remains). This is shown in Eqn (2):

#### Untreated waste tyre derived oil according to their collectors.



#### Treated waste tyre derived oil according to their collectors.



**Figure 5.** GC-FPD chromatograms of sulfur compounds in (A) untreated and (B) treated waste tyre rubber crumb-derived oil.



**Table 5.** Pyrolysis mass balance of untreated and treated tyre samples

| Untreated tyre crumbs     |             | Treated tyre crumbs       |             |
|---------------------------|-------------|---------------------------|-------------|
| Before pyrolysis          | Mass (g)    | Before pyrolysis          | Mass (g)    |
| Overall total             |             | Overall total             |             |
| Volatiles                 | —           | Volatiles                 | —           |
| Fixed carbon/char         | 40          | Fixed carbon/char         | 40          |
| Ash                       | 1.59        | Ash                       | 0.47        |
| Component balance         |             | Component balance         |             |
| Sulfur                    | <b>0.70</b> | Sulfur                    | <b>0.45</b> |
| After pyrolysis at 600 °C |             | After pyrolysis at 280 °C |             |
| Overall total             | Mass (g)    | Overall total             | Mass (g)    |
| Volatiles                 | 24.7        | Volatiles                 | 19.9        |
| Fixed carbon/char         | 15.3        | Fixed carbon/char         | 20.1        |
| Ash                       | 1.96        | Ash                       | 1.02        |
| Component balance         |             | Component balance         |             |
| Sulfur (solids)           | <b>0.53</b> | Sulfur (solids)           | <b>0.17</b> |
| Sulfur (liquid)           | <b>0.17</b> | Sulfur (liquid)           | <b>0.04</b> |
| Sulfur <sup>a</sup> (gas) | <b>0.01</b> | Sulfur <sup>a</sup> (gas) | <b>0.24</b> |

<sup>a</sup> Calculated by difference.

$$F_s = V_{(O+G)s} + C_s \quad (2)$$

where  $F$  is feed,  $V$  is volatiles and  $C$  is char, with  $O$  being oil and  $G$  gas.

Mass balance distribution was calculated using the mass in grams to specifically track the amount of sulfur in the solid, liquid and gas produced. The masses were converted from weight percentage to grams for easy calculation. Equation (3) was used to convert the masses:

$$\frac{\text{Mass}_{\text{wt}\%}}{100} \times \text{Mass}_g \quad (3)$$

Table 5 summarizes the results obtained from mass balance in grams. The sulfur distribution in mass was established according to the categories of the mass before (solid) and after (solid, liquid and gas) pyrolysis. From the treated tyre results obtained, it can be seen that there is more sulfur in the gas product than in solid and liquid products. This suggests that more sulfur was released in the form of gas therefore more sulfur–sulfur bonds were broken during the treatment, converted to  $\text{SO}_2$  and  $\text{H}_2\text{S}$  gases during pyrolysis. While for the untreated tyre crumbs there was more sulfur in the solid product than in the liquid and gas products. This shows the success of the chemical treatment, as the objective is to reduce the sulfur content in the TDO. Approximately 0.3 g of sulfur was cut during the chemical treatment alone and only about 0.04 g is present in the liquid product. It can also be seen that about 24% of overall sulfur was present in the untreated TDO after pyrolysis as compared to about 10% overall sulfur remaining in the treated TDO. Also noticed was that for untreated waste tyre rubber crumbs, more sulfur remained in the solid product,

**Table 6.** Summary of the study

| Untreated waste tyre rubber crumbs | Treated waste tyre rubber crumbs |
|------------------------------------|----------------------------------|
| 54.5% oil yield                    | 46% oil yield                    |
| Pungent/tyre oil smell             | Petroleum oil smell              |
| High PAHs                          | PAHs reduced by 83%              |
| 0.17 g sulfur oil                  | 0.04 g sulfur in oil             |
| 0.53 g sulfur in char              | 0.17 g sulfur in char            |

**Table 7.** Advantages of chemical treatment pyrolysis

|  | Conventional (slow) pyrolysis               | Chemical treatment pyrolysis   |
|--|---|--|
| Temperature                              | 400–1000 °C                                 | 100–280 °C   |
| High temperature and long residence time | High temperature and long residence time    | Low temperature and short residence time   |
| Products                                 | High sulfur, high PAH content; (tyre) odour | Low sulfur, low PAH content; petroleum odour   |
| Sustainability                           | Non-renewable                               | Semi-renewable (solvent is recovered and reused)/ reduced energy required for waste tyre pyrolysis |
| Cost                                     | High  | Relatively cost-effective  |
| Environmental harm                       | High to medium                              | Medium to low  |

whereas for the treated waste tyre most sulfur left in gas form. Therefore, this means that not only is the oil produced from treated waste tyre rubber crumb better in quality than that produced from untreated waste tyre rubber crumb, but also the char produced from treated waste tyre rubber crumb is comparatively better.

## CONCLUSIONS

This study was focused on the improvement of waste tyre rubber crumb pyrolysis in terms of finding a better way to perform pyrolysis at a lower temperature and at the same time improve the quality of oil produced. Chemical treatment of waste tyre rubber crumbs before pyrolysis was proposed as an alternative way. The optimization of pyrolysis conditions was done following the controlled variable principle, the optimized conditions were determined and a maximum of about 46 wt% oil was produced for pre-treated samples, compared to about 55% for untreated samples. Untreated TDO produced had a pungent tyre odour, while treated TDO had a petroleum smell. GC–MS analysis showed that treated TDO had a smaller amount of PAHs than TDO from untreated tyre crumb. As for sulfur content, it was reduced by about 94% in the treated TDO from untreated tyre crumb before pyrolysis. This study was successful in achieving the aims and objectives of this research. Table 6 summarizes the results obtained as per the aims and objectives of this study.

Table 7 sums up the benefits of using chemical pre-treatment of waste tyres before pyrolysis as compared to conventional

pyrolysis. This study showed that chemical treatment pyrolysis requires low temperature, the process takes less time to complete and small amounts of sulfur and PAHs are produced from the oil. Therefore, this process automatically will be cheaper to perform as compared to conventional pyrolysis. Furthermore, pyrolysing treated waste tyres will bring less harm to the environment because of the following discovered facts:

- Treated waste tyre crumbs had less sulfur content as compared to untreated tyre crumbs; therefore smaller amounts of sulfur gases are released as compared to conventional pyrolysis.
- There are fewer or no PAHs released during pyrolysis process because, as reported in the literature, these compounds are formed at higher temperatures.<sup>21</sup> This study showed that fewer PAHs were formed during the pyrolysis of treated waste tyres.

The following are the recommendations from this study: the use of real-time GC–MS to monitor gases released during treatment (identification of gases released – understand for possible application). The same technique to be used for the pyrolysis process to help understand the mechanism of decomposition reactions taking place. Also to be explored is the use of a scrubber system as air pollution control device during pyrolysis.

## AUTHOR CONTRIBUTIONS

PCT and SPH conceived the research; PCT performed the experiments; PCT, MMP, SAI, NMM, MJP and SPH analysed the data, discussed the results and drew the conclusions; PCT wrote the original manuscript draft; MMP, SAI, NMM, MJP and SPH reviewed and edited the manuscript; supervision, SAI, NMM and SPH.

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## COMPETING INTERESTS

The authors declare no competing interests.

## SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

## REFERENCES

- Mmerekhi D, Machola B and Mokokwe K, Status of waste tires and management practice in Botswana. *J Air Waste Manage Assoc* **69**:1230–1246 (2019). <https://doi.org/10.1080/10962247.2017.1279696>.
- Markl E and Lackner M, Devulcanization technologies for recycling of tire-derived rubber: a review. *Materials* **13**:1246 (2020). <https://doi.org/10.3390/ma13051246>.
- Chen F and Qian J, Studies on the thermal degradation of *cis*-1,4-polyisoprene. *Fuel* **81**:2071–2077 (2002). [https://doi.org/10.1016/S0016-2361\(02\)00147-3](https://doi.org/10.1016/S0016-2361(02)00147-3).
- Abdul-Raouf ME, Maysour NE, Abdul-Azim AA and Amin MS, Thermochemical recycling of mixture of scrap tyres and waste lubricating oil into high calorific value products. *Energy Convers Manage* **51**:1304–1310 (2010). <https://doi.org/10.1016/j.enconman.2010.01.007>.
- Idehai IM and Akujieze CN, Assessment of some physiochemical impacts of municipal solid waste (MSW) on soils: a case study of landfill areas of Lagos, Nigeria. *Br J Appl Sci Technol* **4**:4623 (2014). <https://doi.org/10.9734/BJAST/2014/12964>.
- Singh A, Spak SN, Stone EA, Downard J, Bullard RL, Pooley M *et al.*, Uncontrolled combustion of shredded tires in a landfill – part 2: population exposure, public health response, and an air quality index for urban fires. *Atmos Environ* **104**:273–283 (2015). <https://doi.org/10.1016/j.atmosenv.2015.01.002>.
- Di Trapani D, Di Bella G and Viviani G, Uncontrolled methane emissions from a MSW landfill surface: influence of landfill features and side slopes. *Waste Manage* **33**:2108–2115 (2013). <https://doi.org/10.1016/j.wasman.2013.01.032>.
- Antoniou N and Zabaniotou A, Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery. *Renewable Sustainable Energy Rev* **20**:539–558 (2013). <https://doi.org/10.1016/j.rser.2012.12.005>.
- Yaqoob H, Teoh YH, Sher F, Jamil MA, Murtaza D, Al Qubeissi M *et al.*, Current status and potential of tire pyrolysis oil production as an alternative fuel in developing countries. *Sustainability* **13**:3214 (2021). <https://doi.org/10.3390/su13063214>.
- Yazdani E, Hashemabadi SH and Taghizadeh A, Study of waste tire pyrolysis in a rotary kiln reactor in a wide range of pyrolysis temperature. *Waste Manage* **85**:195–201 (2019). <https://doi.org/10.1016/j.wasman.2018.12.020>.
- Xu S, Lai D, Zeng X, Zhang L, Han Z, Cheng J *et al.*, Pyrolysis characteristics of waste tire particles in fixed-bed reactor with internals. *Carbon Resour Convers* **1**:228–237 (2018). <https://doi.org/10.1016/j.wasman.2013.05.003>.
- Banar M, Akyildiz V, Özkan A, Çokaygil Z and Onay Ö, Characterization of pyrolytic oil obtained from pyrolysis of TDF (tire derived fuel). *Energy Convers Manage* **62**:22–30 (2012). <https://doi.org/10.1016/j.enconman.2012.03.019>.
- Wey MY, Liou BH, Wu SY and Zhang CH, The autothermal pyrolysis of waste tires. *J Air Waste Manage Assoc* **45**:855–863 (1995). <https://doi.org/10.1080/10473289.1995.10467415>.
- Benallal B, Roy C, Pakdel H, Chabot S and Poirier MA, Characterization of pyrolytic light naphtha from vacuum pyrolysis of used tyres comparison with petroleum naphtha. *Fuel* **74**:1589–1594 (1995). [https://doi.org/10.1016/0016-2361\(95\)00165-2](https://doi.org/10.1016/0016-2361(95)00165-2).
- Pakdel H, Roy C, Aubin H, Jean G and Coulombe S, Formation of dl-limonene in used tire vacuum pyrolysis oils. *Environ Sci Technol* **25**:1646–1649 (1991). <https://doi.org/10.1021/es00021a018>.
- Cunliffe AM and Williams PT, Composition of oils derived from the batch pyrolysis of tyres. *J Anal Appl Pyrolysis* **44**:131–152 (1998). [https://doi.org/10.1016/S0165-2370\(97\)00085-5](https://doi.org/10.1016/S0165-2370(97)00085-5).
- Hita I, Arabiourrutia M, Olazar M, Bilbao J, Arandes JM and Castaño P, Opportunities and barriers for producing high quality fuels from the pyrolysis of scrap tires. *Renewable Sustainable Energy Rev* **56**:745–759 (2016). <https://doi.org/10.1016/j.rser.2015.11.081>.
- Campuzano F, Jameel AG, Zhang W, Emwas AH, Agudelo AF, Martínez JD *et al.*, On the distillation of waste tire pyrolysis oil: a structural characterization of the derived fractions. *Fuel* **290**:120041 (2021). <https://doi.org/10.1016/j.fuel.2020.120041>.
- Danon B, Van Der Gryp P, Schwarz CE and Görgens JF, A review of dipentene (dl-limonene) production from waste tire pyrolysis. *J Anal Appl Pyrolysis* **112**:1–13 (2015). <https://doi.org/10.1016/j.jaap.2014.12.025>.
- dos Santos RG, Rocha CL, Felipe FL, Cezario FT, Correia PJ and Rezaei-Gomari S, Tire waste management: an overview from chemical compounding to the pyrolysis-derived fuels. *J Mater Cycles Waste Manage* **22**:628–641 (2020). <https://doi.org/10.1007/s10163-020-00986-8>.
- Ngxangxa S, Development of GC-MS methods for the analysis of tyre pyrolysis oils. Doctoral dissertation, Stellenbosch University, Stellenbosch (2016). <http://hdl.handle.net/10019.1/98868>.
- Ding K, Zhong Z, Zhang B, Song Z and Qian X, Pyrolysis characteristics of waste tire in an analytical pyrolyzer coupled with gas chromatography/mass spectrometry. *Energy Fuels* **29**:3181–3187 (2015). <https://doi.org/10.1021/acs.energyfuels.5b0024>.
- Williams PT, Pyrolysis of waste tyres: a review. *Waste Manage* **33**:1714–1728 (2013). <https://doi.org/10.1016/j.wasman.2013.05.003>.
- Williams PT, Besler S and Taylor DT, The batch pyrolysis of tyre waste: fuel properties of the derived pyrolytic oil and overall plant economics. *Proc Inst Mech Eng A* **207**:55–63 (1993). [10.1243/PIME\\_PROC\\_1993\\_207\\_007\\_02](https://doi.org/10.1243/PIME_PROC_1993_207_007_02).
- Duan P, Jin B, Xu Y and Wang F, Co-pyrolysis of microalgae and waste rubber tire in supercritical ethanol. *Chem Eng J* **269**:262–271 (2015). <https://doi.org/10.1016/j.cej.2015.01.108>.

- 26 Shah SA, Zeeshan M, Farooq MZ, Ahmed N and Iqbal N, Co-pyrolysis of cotton stalk and waste tire with a focus on liquid yield quantity and quality. *Renewable Energy* **130**:238–244 (2019). <https://doi.org/10.1016/j.renene.2018.06.045>.
- 27 Martínez JD, Veses A, Mastral AM, Murillo R, Navarro MV, Puy N *et al.*, Co-pyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. *Fuel Process Technol* **119**:263–271 (2014). <https://doi.org/10.1016/j.fuproc.2013.11.015>.
- 28 Zhang X, Lei H, Chen S and Wu J, Catalytic co-pyrolysis of lignocellulosic biomass with polymers: a critical review. *Green Chem* **18**:4145–4169 (2016). <https://doi.org/10.1039/C6GC00911E>.
- 29 Singh M, Salaudeen SA, Gilroyed BH, Al-Salem SM and Dutta A, A review on co-pyrolysis of biomass with plastics and tires: recent progress, catalyst development, and scaling up potential. *Biomass Convers Biorefin*:1–25 (2021). <https://doi.org/10.1007/s13399-021-01818-x>.
- 30 Arabiourrutia M, Lopez G, Artetxe M, Alvarez J, Bilbao J and Olazar M, Waste tyre valorization by catalytic pyrolysis: a review. *Renewable Sustainable Energy Rev* **129**:109932 (2020). <https://doi.org/10.1016/j.rser.2020.109932>.
- 31 Ayanoğlu A and Yumrutaş R, Production of gasoline and diesel like fuels from waste tire oil by using catalytic pyrolysis. *Energy* **103**:456–468 (2016). <https://doi.org/10.1016/j.energy.2016.02.155>.
- 32 Banihani FF and Hani ZF, The effect of catalyst ratio on the pyrolysis yields for waste tyre. *Am J Chem Eng* **6**:60–64 (2018). <https://doi.org/10.11648/j.ajche.20180604.14>.
- 33 Ahoor AH and Zandi-Atashbar N, Fuel production based on catalytic pyrolysis of waste tires as an optimized model. *Energy Convers Manage* **87**:653–669 (2014). <https://doi.org/10.1016/j.enconman.2014.07.033>.
- 34 Osayi JI and Osifo P, Utilization of synthesized zeolite for improved properties of pyrolytic oil derived from used tire. *Int J Chem Eng* **2019**:6149189 (2019). <https://doi.org/10.1155/2019/6149189>.
- 35 Jantaraksa N, Prasassarakich P, Reubroycharoen P and Hinchiranan N, Cleaner alternative liquid fuels derived from the hydrodesulfurization of waste tire pyrolysis oil. *Energy Convers Manage* **95**:424–434 (2015). <https://doi.org/10.1016/j.enconman.2015.02.003>.
- 36 Bett RK, Kumar A and Siagi ZO, Optimization of liquid fuel production from microwave pyrolysis of used tyres. *J Energy* **2021**:1–11 (2021). <https://doi.org/10.1155/2021/3109374>.
- 37 Tsipa PC, Method development for chemolysis of waste tyres and characterization of the components. MSc dissertation, Nelson Mandela University (2018) Available: [http://vital.seals.ac.za:8080/vital/access/manager/Repository/vital:34044?site\\_name=GlobalView](http://vital.seals.ac.za:8080/vital/access/manager/Repository/vital:34044?site_name=GlobalView).
- 38 Skogestad S, Plantwide control: the search for the self-optimizing control structure. *J Process Control* **10**:487–507 (2000). [https://doi.org/10.1016/S0959-1524\(00\)00023-8](https://doi.org/10.1016/S0959-1524(00)00023-8).
- 39 Alsaleh A and Sattler ML, Waste tire pyrolysis: influential parameters and product properties. *Renewable Energy Rep* **1**:129–135 (2014). <https://doi.org/10.1007/s40518-014-0019-0>.
- 40 Varkey JT, Augustine S and Thomas S, Thermal degradation of natural rubber/styrene butadiene rubber latex blends by thermogravimetric method. *Polym-Plast Technol Eng* **39**:415–435 (2000). <https://doi.org/10.1081/PPT-100100038>.
- 41 Sun Y, Bai F, Liu B, Liu Y, Guo M, Guo W *et al.*, Characterization of the oil shale products derived via topochemical reaction method. *Fuel* **115**:338–346 (2014). <https://doi.org/10.1016/j.fuel.2013.07.029>.
- 42 Sun YH, Bai FT, Lü XS, Li Q, Liu YM, Guo MY *et al.*, A novel energy-efficient pyrolysis process: self-pyrolysis of oil shale triggered by topochemical heat in a horizontal fixed bed. *Sci Rep* **5**:8290 (2015). <https://doi.org/10.1038/srep08290>.
- 43 Harrison KL, Johnston KP and Sanchez IC, Effect of surfactants on the interfacial tension between supercritical carbon dioxide and polyethylene glycol. *Langmuir* **12**:2637–2644 (1996). <https://doi.org/10.1021/la9510137>.
- 44 Chen G and Fang B, Preparation of solid acid catalyst from glucose-starch mixture for biodiesel production. *Bioresour Technol* **102**:2635–2640 (2011). <https://doi.org/10.1016/j.biortech.2010.10.099>.
- 45 Babel K, Porous structure evolution of cellulose carbon fibres during heating in the initial activation stage. *Fuel Process Technol* **85**:75–89 (2004). [https://doi.org/10.1016/S0378-3820\(03\)00109-](https://doi.org/10.1016/S0378-3820(03)00109-)
- 46 Mujeebu MA, Abdullah MZ, Bakar MA, Mohamad AA and Abdullah MK, Applications of porous media combustion technology: a review. *Appl Energy* **86**:1365–1375 (2009). <https://doi.org/10.1016/j.apenergy.2009.01.017>.
- 47 Mohamad AA, Combustion in porous media: fundamentals and applications, in *Transport Phenomena in Porous Media III*. Pergamon, Oxford, UK, pp. 287–304 (2005).
- 48 Intapun J, Rungruang T, Suchat S, Cherdchim B and Hiziroglu S, The characteristics of natural rubber composites with Klason lignin as a green reinforcing filler: thermal stability, mechanical and dynamical properties. *Polymers* **13**:1109 (2021). <https://doi.org/10.3390/polym13071109>.
- 49 Burgaz E, Gencoglu O and Gokuzoglu M, Carbon black reinforced natural rubber/butadiene rubber and natural rubber/butadiene rubber/styrene-butadiene rubber composites: part I: rheological, mechanical and thermomechanical properties. *Res Eng Struct Mater* **5**:233 (2019). <https://doi.org/10.17515/resm2019.74ma1123>.
- 50 Wang Z, Burra KG, Zhang M, Li X, Policella M, Lei T *et al.*, Co-pyrolysis of waste tire and pine bark for syngas and char production. *Fuel* **274**:117878 (2020). <https://doi.org/10.1016/j.fuel.2020.117878>.
- 51 Nadal M, Rovira J, Díaz-Ferrero J, Schuhmacher M and Domingo JL, Human exposure to environmental pollutants after a tire landfill fire in Spain: health risks. *Environ Int* **97**:37–44 (2016). <https://doi.org/10.1016/j.envint.2016.10.016>.
- 52 Mitchell CJ, Niebyski ML, Smith GC, Karatsos N, Martin D, Mutebi JP *et al.*, Isolation of eastern equine encephalitis virus from *Aedes albopictus* in Florida. *Science* **257**:526–527 (1992). <https://doi.org/10.1126/science.1321985>.
- 53 Downard J, Singh A, Bullard R, Jayarathne T, Rathnayake CM, Simmons DL *et al.*, Uncontrolled combustion of shredded tires in a landfill – part 1: characterization of gaseous and particulate emissions. *Atmos Environ* **104**:195–204 (2015). <https://doi.org/10.1016/j.atmosenv.2014.12.059>.
- 54 Olson DB and Pickens JC, The effects of molecular structure on soot formation. I. Soot thresholds in premixed flames. *Combust Flame* **57**:199–208 (1984). [https://doi.org/10.1016/0010-2180\(84\)90057-9](https://doi.org/10.1016/0010-2180(84)90057-9).