A novel chemical pre-pyrolysis treatment of waste tyre crumbs: A viable way for low temperature waste tyre pyrolysis

Phuti Cedrick Tsipa [a,b,*], Mapoloko Mpho Phiri [a], Samuel Ayodele Iwarere [c,**], Ntandoyenkosi Malusi Mkhize [b], Mohau Justice Phiri [d], Shanganyane Percy Hlangothi [a]

[a] Nelson Mandela University, Centre for Rubber Science & Technology, Department of Chemistry, P.O. Box 77000, Port Elizabeth 6301,South Africa
[b] University of KwaZulu-Natal, Chemical Engineering Discipline, 348 Mazisi Kunene Road, Glenwood 4041, South Africa
[c] University of Pretoria, Department of Chemical Engineering, Faculty of Engineering, Built Environment, and Information Technology, Lynnwood Road, Hatfield, Pretoria 0028, South Africa
[d] Vaal University of Technology, Department of Natural Science, Private Bag X021, Vanderbijlpark, South Africa

ARTICLE INFO

ABSTRACT

Pyrolysis of tyres is a process that consumes non-renewable energy resources, and is characterised by the requirement of a significant amount of energy. For example, natural rubber and styrene-butadiene rubber require 300–350 °C and 400–450 °C, respectively, to decompose under inert nitrogen conditions. The current study aims, firstly, to reduce the temperature typically used for waste tyre crumbs pyrolysis to minimise the energy requirement of the process as well as to improve the quality of the liquid fraction of the pyrolysis product, tyre derived oil, (TDO). Before pyrolysis, waste tyre crumbs were first treated with a mixture of chemicals, dried and then pyrolysed using a 40 g vertical fixed bed reactor. The results acquired from the ultimate analyser for the CHNS illustrated a decrease in carbon from 80.6 % to 57.2 % and an increment in nitrogen (from 0.4 % to 6.5 %) and oxygen (from 9.7 % to 30.2 %) in the treated tyre crumbs. FTIR results indicated that oxidation took place in the treated sample by displaying the presence of oxygenated functional groups in the spectrum, which agreed with CHNS results. The temperature was reduced drastically from a minimum of 400 °C to a minimum of 100 °C for pyrolysis, and therefore, resulting in a lower initial/starting pyrolysis temperature range of 100–115 °C. In addition, approximately 87 wt% pyrolysis yield was obtained out of 60 % pyrolysable substances in a tyre at the final temperature of 280 °C. The differential thermogravimetric analyser (DTA) was used to confirm the extent to which pyrolysis experiments took place in the feedstock by analysing the char after pyrolysis. The current study is set to improve the pyrolysis of waste tyre crumbs by significantly reducing the temperature and time of the process, which lowers the operation cost required for the tyre crumbs' pyrolysis process.

1. Introduction

Pyrolysis involves heating a carbon-containing material at high temperatures between 400 and 1000 °C in the absence of oxygen, resulting in the breakdown to its constituent chemical components [1, 2]. There are different types of pyrolysis reactors which can be classified into three categories: pneumatic bed, mechanical and gravity pyrolysis reactors. Pneumatic bed reactor cluster consists of fluidized bed and fixed bed reactors. These reactors provide the following advantages:

- Shield and protect the organic material from oxidation.
- Gas flow affects the contact time of the vapor and hot char which influences the severity of secondary reactions. It also evens out the temperature and concentration distribution.
- Discharges volatile pyrolysis products.
- Sometimes, it is also a carrier of thermal energy.
- The behavior of the bed in the pyrolyser depends on both the inert gas flow rate and the size and specific gravity of tyre particles; meaning when the inert gas flow is slow, the solid particles remain stationary in the bed: this is fixed-bed pyrolysis [3–5].

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* Corresponding author at: Nelson Mandela University, Centre for Rubber Science & Technology, Department of Chemistry, P.O. Box 77000, Port Elizabeth 6301, South Africa.
** Corresponding author.
E-mail addresses: s215375548@mandela.ac.za (P.C. Tsipa), samuel.iwarere@up.ac.za (S.A. Iwarere).

Table 1

SAPIA [18] sulphur and aromatics content regulations in fuels.

Gasoline		
	CF1 (2006)	CF2 (n.d)
Sulphur (ppm)	500	10
Aromatic (vol%)	50	35
Diesel		
Sulphur (ppm)	500/50	10
PAHs (% mass)	Not specific	11

Where: CF denotes Cleaner Fuel

Table 2

Comparison between conventional waste tyre pyrolysis and solvent-treated waste tyre pyrolysis [23].

	Conventional (slow) pyrolysis	Solvent treatment pyrolysis
Temperature	400–1000 °C	100–280 °C
	High temperature and long residence time	Low temperature and short residence time
Products	High sulphur, High PAHs content and (tyre) Odour	Low sulphur, low PAHs, and petroleum odour
Sustainability	Non-renewable	Semi-renewable (solvent is recovered and reused)/reduce the energy required for waste tyres pyrolysis
Cost	High	Expected to be cost-effective (to be confirmed)

Table 3

Proximate and elemental analysis of the untreated waste tyre crumb (UWT).

Proximate analysis of untreated rubber crumb			
Moisture (%)	Volatile (%)	Fixed carbon (%)	Ash (%)
2.29	57.75	35.98	3.98
Elemental analysis of untreated rubber crumb			
Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)
80.62	7.46	0.42	1.76
*Oxygen = 9.74 % (calculated by difference)			

The mechanical rector cluster consist of auger, rotary and ablation (/with stirrer) pyrolysis reactors. These are continuous processes which are most advantageous since more tyres can be pyrolysed daily. The conditions for a high oil yield is a fast-heating rate of the charge during the process, which depends on the gas-solid contact mode. Unlike pneumatic charge transport, the focus is on the apparatus in which the contact between the waste tyres and heating agent is brought about mechanically, and this contact affects oil properties [6,7]. Finally, gravity pyrolysis reactors consist of column type reactors.

One of the simplest and cheapest ways to achieve the transportation of the feedstock is to use the force of gravity [8–10]. Pyrolysers with gravitational batch transport use gravitational force in a continuous vacuum pyrolyser to dispense and move shredded cross-ply tyres from the feeder into the pyrolyser through a double sluice and inside the reactor [9]. The organic vapours (hydrocarbon gases and liquids) are sucked out and removed from the reactor chamber by a mechanical vacuum pump and condensed in a series of condensers. These reactors have a great influence on the oil and gas yields, and the quality of the char produced

The thermal decomposition process has gained traction worldwide as one of the most efficient ways of recycling waste tyres. The recovered useful products are in the form of gas, liquid, and char/residue. The attractive feature for the pyrolysis of waste tyres is that it is characterised by high amounts of energy density with a calorific value range of 28–40 MJ.kg^{-1}, which is higher than coal and biomass [11]. The respective quantity and quality of pyrolysis products depend on the pyrolysis reactor's heating rate, feedstock composition, particle size, carrier gas flow, and temperature. Of these, temperature is the most predominant factor [12].

The conventional minimum tyre pyrolysis temperature recorded in literature is > 400 °C, below which conversion becomes incomplete [13]. This was demonstrated in a study by de Macro Rodriguez *et al.* [13], who recorded the following conversions for the pyrolysis of waste tyres at 300 °C; solid ∼87.6 %, liquid ∼4.8 %, and gas 7.7 %. Their study also showed a good correlation between temperature and quantity of the liquid product between 300 and 700 °C. Similar findings were reported in other related studies [14–16]. Other than quantity, it has also been reported that pyrolysis at high temperatures has additional benefits. The main one is the production of oil that contains relatively higher concentrations of polycyclic aromatic hydrocarbons (PAHs). Alsaleh *et al.* [14] reported relative lower sulphur content at an intermediate temperature of 550 °C when compared to low temperature of 400 °C and a higher temperature of 650 °C. Ismail *et al.* [17] reported that the bulk of the elemental sulphur and sulphur-containing compounds were recollected in the solid char, while some were found in the light naphtha fraction. The quantity of sulphur and sulphur-containing compounds in oil fractions has become very important as an indicator of fuel quality in many countries. For instance, in South Africa, the South African Petroleum Industry Association (SAPIA) put regulations for sulphur and aromatic content as shown in Table 1 [18,19].

The quality of pyrolytic gases can also be affected by the process temperature. Literature showed that gases produced at low pyrolysis temperatures had much higher calorific values, as high as 81 MJ/Nm^3 when compared to those produced at relatively higher temperatures [20, 21].

Besides temperature, pressure also plays a significant role in the pyrolysis process. Since pressure is directly proportional to temperature, according to the ideal gas law equation (PV = nRT), low-temperature pyrolysis may suggest that pyrolysis is taking place at low pressures, unless specified otherwise. The following are a few advantages of low pressure in the pyrolysis system as documented by Martínez *et al.* [20]; reduced secondary reactions in the gas phase, reduced resident time of the volatiles, and improvement in oil yields. It is worth noting that reduced secondary reactions may reduce gas deposition onto the char produced, leading to better quality char [20].

Therefore, since temperature and pressure dictate the quality and quantity of the pyrolysis products, it is imperative that these factors are considered and explored further in the pursuit to producing pyrolysis products with acceptable/useful quality and quantity at optimally favourable processing conditions. This quest is not new. For example, Ahoor *et al.* [22] showed in their study that by using MgCl$_2$ catalyst, it is possible to use low temperatures, reduce reaction time, and produce the highest liquid yield. However, the use of such inorganic catalysts are costly and degrade in performance with use, which will add more expenses for the regeneration/recovery process.

The current study proposes the pre-treatment of waste tyre granules with a mixture of acid-solvent chemicals as a viable way of enabling low-temperature pyrolysis. The composition of this chemical mixture was experimentally selected based on the proven ability to break the polymer's backbone, toxicity, and associated costs. The success of this study is crucial as it will potentially revolutionise both the tyre recycling and environmental safety research field worldwide. Table 2 summarises the benefits of the waste tyre treatment before pyrolysis compared to conventional pyrolysis.

2. Materials and methods

2.1. Tyre crumbs pre-treatment

The pre-treatment method used a solvent chemical mixture of protonic acid (supplied by MERCK, 69 % purity) and organic solvent (supplied by MERCK, laboratory grade), with the acid to solvent ratio of 5 mL: 95 mL. The application followed the phase transfer principle with
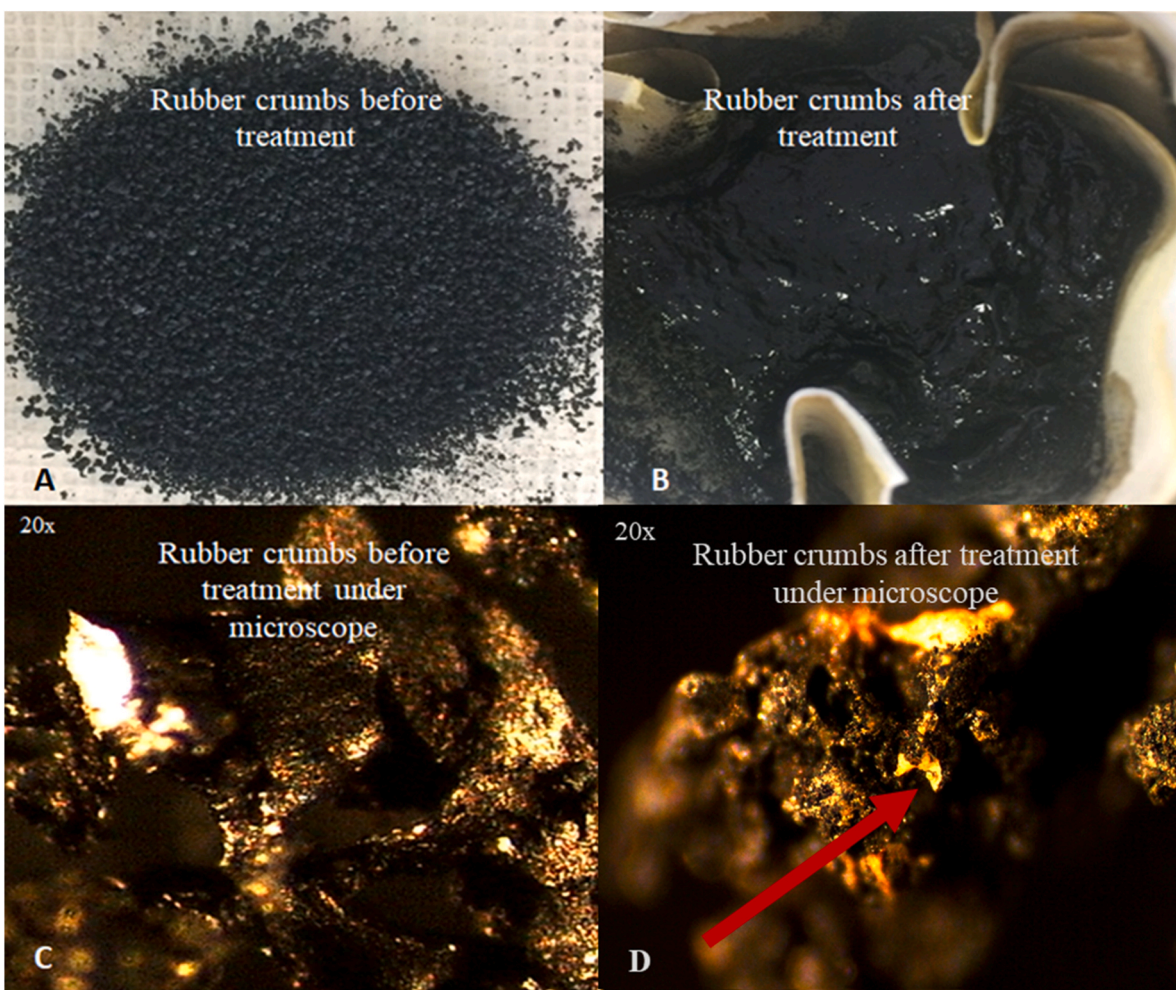
Fig. 1. Pictorials of rubber crumbs from pre- to post-treatment. A- 30 mesh rubber crumbs: untreated, B – rubber crumbs after chemical treatment (before drying), C – 30 mesh rubber crumbs: untreated under light microscope (20x magnification) and D – rubber crumbs after chemical treatment then dried, viewed under light microscope (20x magnification).
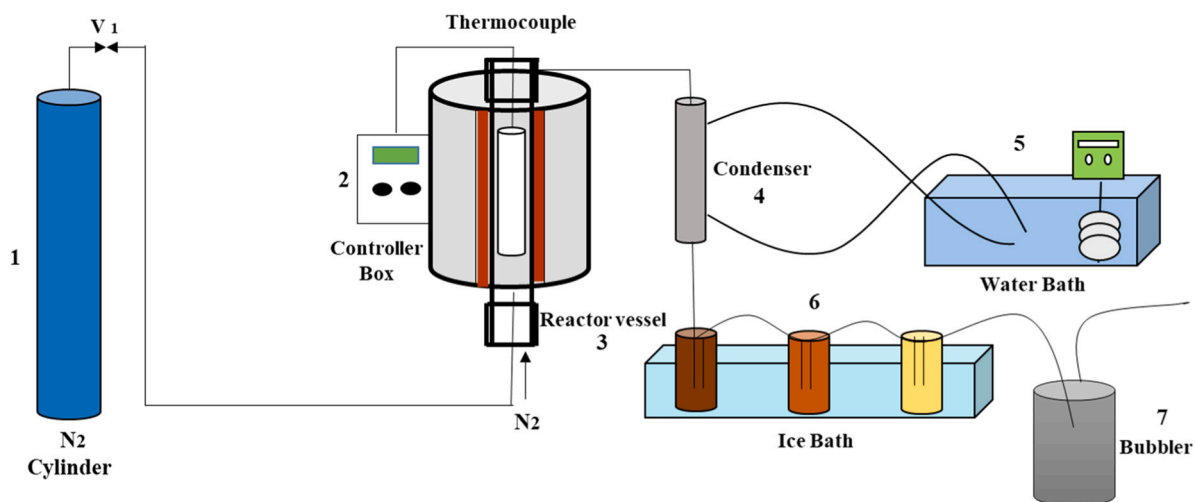

Fig. 2. Pyrolysis unit layout: Unit 1 – nitrogen cylinder, unit 2 – controller box, unit 3 - reactor vessel consisting of heating jacket and reactor, unit 4 – condenser, unit 5 – water bath equipped with a heating element, unit 6 – ice bath with 3 collectors and unit 7 – bubbler with water to filter fumes [15].

the rubber crumb ratio of 1:4 solvent chemical mixture. Coarse sand with particle size range of 30–40 mesh was used as a blank sample due to its non-volatility and untreated rubber crumb as reference for comparison. Other solvent mixtures (acids and organic solvents) tested in this study are also detailed in supplementary material Table S1 under sub-heading SM-1. The sample's proximate and elemental analysis
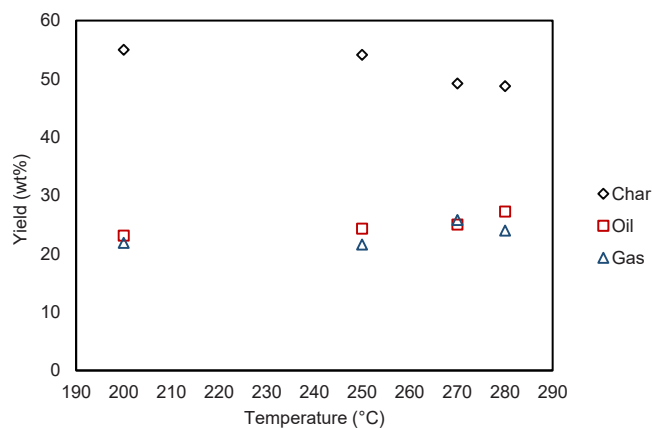
Fig. 3. Effect of pyrolysis temperature on the yields of solid, liquid, and gaseous products.

properties of the untreated rubber crumb are reported in Table 3.

The pre-treatment procedure involved soaking waste tyre rubber crumbs (30 mesh) in a chemical mixture and stirred for 2–3 hours in ambient conditions. The solid substance was thereafter separated from the liquid by using vacuum filtration 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 ± 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 on random errors which may occur in this method.

The solid residual from the treatment was dried in air, and the pictorials showing pre- and post-treatment samples can be seen in Fig. 1. Low molecular weight polymer/heavy oil seemed to have dried up on the surface of the treated rubber crumb. This was confirmed using a NIKON Eclipse E400 light microscope equipped with a camera and a metratherm at 20x magnification. In addition, it was observed in image D that pores formed on the surface of the treated rubber crumbs. Such porosity has been reported to be advantageous to the pyrolysis system as it allows heat diffusion into the inner matrix of the treated rubber crumb [24].

2.2. Pyrolysis unit

The layout of the fixed-bed vertical pyrolysis reactor unit used in this study is shown in Fig. 2. Due to the pyrolytic liquid vapour's corrosive nature, the reactor, sample holder and condenser were designed using stainless steel. Nitrogen cylinder (unit 1) used for keeping the system inert and pushing the pyrolytic vapours to the condenser. The control box (unit 2) used for temperature and heating rate settings. The reactor vessel (Unit 3) consists of three main parts, cylindrical heating jacket with a length of 55.5 cm, the wall thickness of 9 cm and the inner diameter of 4.4 cm; stainless steel cylinder reactor with a length of 57 cm, thickness of 2 mm and the inner diameter of 4 cm, and stainless-steel sample holder with a 40 g capacity, 42.5 cm length cylinder and 28 cm depth to prevent the sample from sitting at the bottom.

2.2.1. Condensation unit

A water-cooled counter-flow condenser (Unit 4) connected to a temperature-controlled water bath (Unit 5) was used for pyrolysis vapour cooling. A temperature-controlled water bath was connected to cool the water pump through the condenser. The internal diameter of the condenser is 1.5 cm with the outer length of 26.5 cm. The condenser was constructed using stainless steel for the same reason that the pyrolytic liquid vapour is corrosive. The water bath (unit 5) temperature was set to 25 °C to avoid the conversion of pyrolytic vapour to oil in the condenser.

2.2.2. Oil collectors and water bubbler

Three oil collectors (Unit 6) were placed in the ice bath to quench pyrolysis vapour at lower temperatures ranging between 3 and 5 °C to maximise the liquid product. This was done to trap as much pyrolysis vapours as possible including light oil fractions. The vapours that escaped the oil collectors went to the water bubbler (Unit 7) to help trap as much harmful gases as possible. The water bubbler was connected to the system for health (safety) purposes and to reduce the environmental risks.

2.2.3. Pyrolysis unit operation

The mass of the nitrogen flow rate pumped into the reactor per second was calculated using the volumetric flow rate. The nitrogen cylinder regulator was used to regulate the gas flow and measure the volumetric flow rate. Mass flow rate ($\dot{m}$) is equal to the volumetric flow rate ($\ddot{V}$) multiplied by the density of the fluid in this case.

$$\dot{m} = \rho \times \ddot{V} \tag{1}$$

$$\dot{m} = 1.2 \times 10^{-4} \quad \frac{kg}{s}$$

The sand was used as a blank to test the reactor's efficiency because of its stability under high-temperature pyrolysis conditions. The reactor was set to 550 °C with a nitrogen volumetric flow rate of 6 l/min.

2.3. Experimental apparatus

The characterisations employed to carry out the aim of this current study are as follows. The functional groups of the treated and untreated rubber crumbs were analysed using Bruker ATR-single reflection diamond crystal (ATR-FTIR) while the surface morphology of the samples was analysed using scanning electron microscope (SEM), JSM-IT 100 equipped with JEOL Scanning Electron Microscope (SEM) technologies. Thermal analysis was done using Shimadzu DTG-60AH (2014 model) simultaneous DTA-TG and TA simultaneous DSC-TGA (SDT) Q600 instruments. DTA-TG was used for monitoring pyrolysis and DSC-TGA (SDT) for proximate analysis. Elemental analysis of the sample was done using Thermo-Scientific Flash 2000 coupled to LC premier micro-mass spectrometer. The resulting oil was characterised using GC-MS and GC-FPD for compounds identity and sulphur content.

3. Results and discussion

3.1. Effect of temperature on the yield of treated rubber crumb oil

It is well-known that natural rubber (NR) decomposes at a temperature range of 300 – 350 °C, and styrene-butadiene (SBR) decomposes at 350 – 450 °C [25] These two rubbers are about 50 % of a tyre composition and form a larger part of the pyrolyzable substance in waste tyres. To test the hypothesis of this study, temperatures below 300 °C were chosen. This was done to ensure that the temperature input from the pyrolysis reactor does not affect the waste tyre sample to prove with certainty that chemical treatment indeed broke the polymer backbone of the waste tyre. Fig. 3 shows the effect of temperature on pyrolysis of treated rubber crumbs. It can be observed that the oil obtained is almost similar to the gas produced. This might be caused by the following reasons: chemical treatment broke the polymer backbone into shorter chains, when pyrolyzed, the chain broke further to form more gas or collectors were not cold enough to condense vapours into liquids and therefore escaped the system as gas.
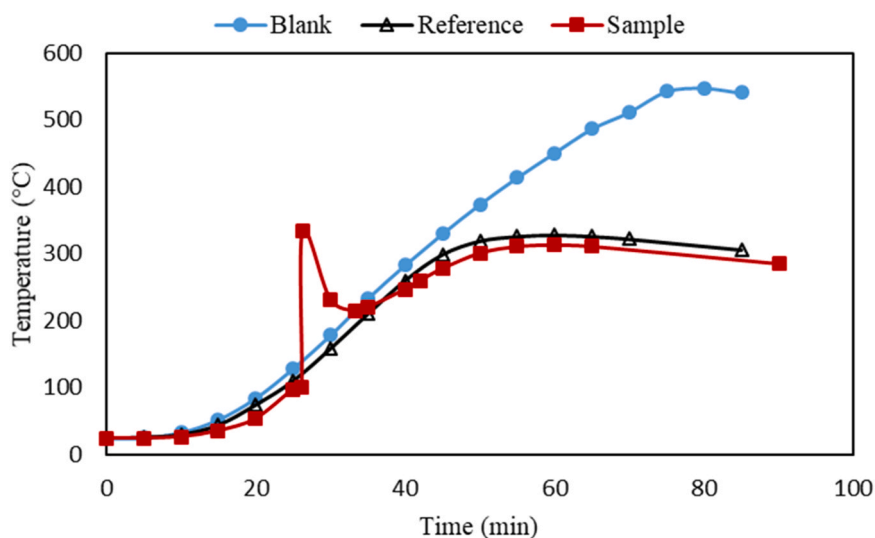
Fig. 4. Pyrolysis temperature-time profile. Summary of temperature history over time to monitor the temperature activity in the reactor.
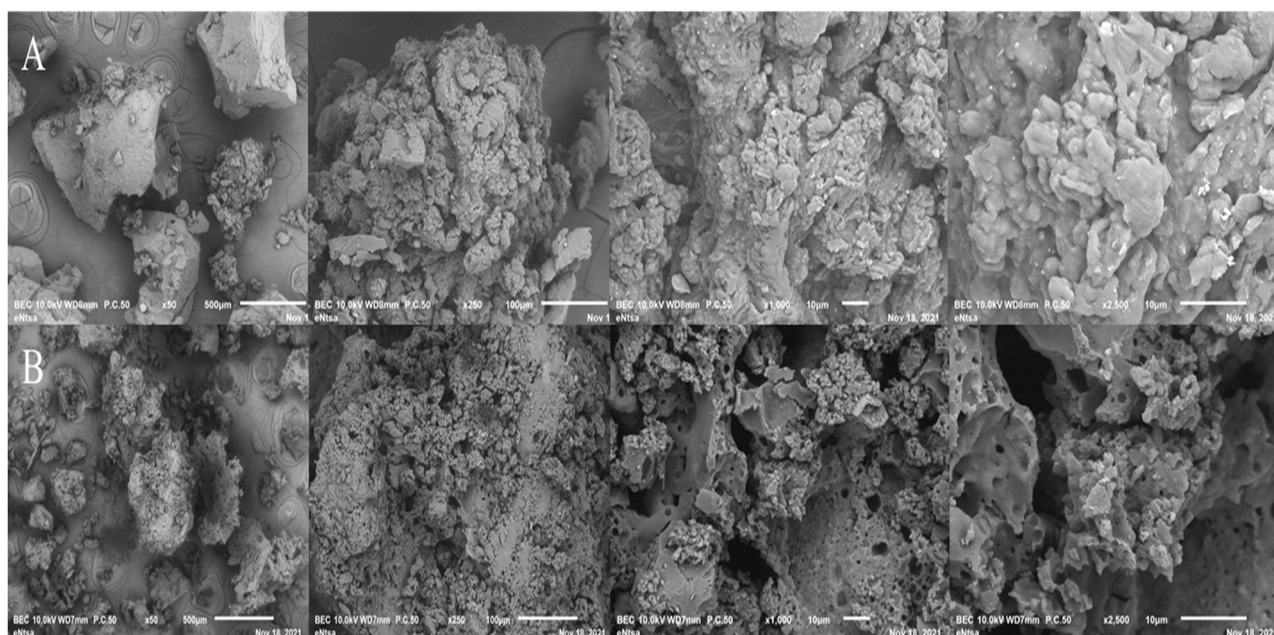

Fig. 5. Sample A: Untreated tyre rubber crumb, Sample B: treated tyre rubber crumb. SEM images at 500 μm; 50×, 250×,1000× and 2500× magnification.

3.2. Temperature – time profile

Forty gram (40 g) feedstock material was subjected to the following pyrolysis program: 6 l/min nitrogen volumetric flow rate, 10 ℃/min heating rate and a final set temperature of 280 ℃ at atmospheric pressure. Temperature - time profile is shown in Fig. 4, were sand represent blank, untreated rubber crumb as reference and treated rubber crumb. Untreated rubber crumbs did not undergo pyrolysis, as could be expected because 280 ℃ is below typical tyre decomposition temperature, instead, only moisture in the rubber crumbs came off.

However, when pre-treated rubber crumbs were subjected to the same conditions, pyrolysis took place. It was observed from the treated tyre crumbs temperature profile that the temperature spiked from around 100 °C to about 334 °C, dropped gradually, and maintained/followed the temperature program thereafter. This incident follows a phenomenon known as self-pyrolysis [26,27]. It is ascribed to resulting from coupling within the oil, oxidation, heat transfer, and gas. During

this process, the autocatalytic system is formed at 100 °C by water-filled pores in the oil resulting in the reduction of energy needed for chemical bond breakage and accelerates the conversion of the pre-treated rubber crumbs [26]. Due to the complete oxidation of light hydrocarbons, temperature increases rapidly. It can also be seen from the temperature program that it took 25–27 min for the temperature to increase from ambient to 100 °C, and only about 1.3 min from 100 °C to 334 °C. The heat released appeared to provide sufficient energy to trigger/propagate reactions and zone expansion. The event's duration was under 9 minutes, during which the oils were rapidly flushed out of the condenser into the oil collector. It was also observed that light oil condensation took less than 5 min to come out of the condenser, whereas heavier oils flowed slowly into the oil collector, taking a couple of hours.

Due to the incident taking place in the treated tyre sample, a closer look at the morphology of the samples was done. Fig. 5 shows SEM images of untreated and treated tyre crumbs before pyrolysis. These

Table 4
Pyrolysis yields (wt%) mean value ± standard deviation of at least three pyrolysis experiments.

	Solid (%)	Liquid (%)	Gas (%)
Blank	98.75 ± 0.1	0	1.25 ± 0.2*
Reference	91.75 ± 1.2	1.5 ± 0.3*	6.75 ± 0.9
Pre-treated sample	48.75 ± 0.5	27.25 ± 0.3	24 ± 0.5

* samples were not dried prior to pyrolysis, therefore gas and liquid from blank and reference resulted due to natural moisture
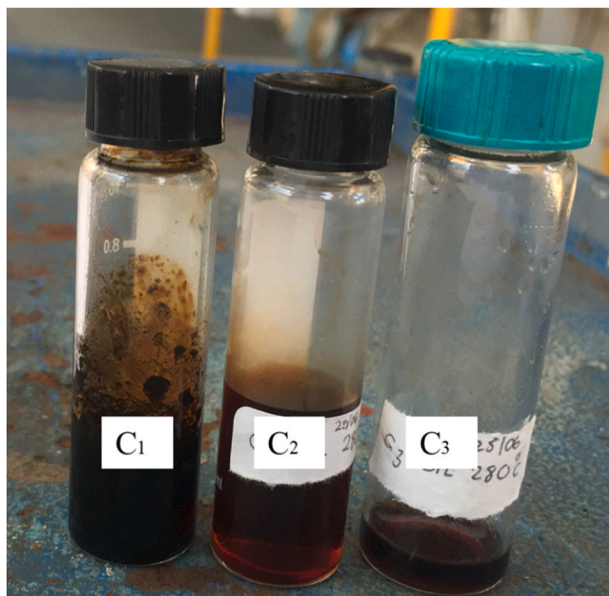

Fig. 6. Oil fractions produced from pre-treated waste tyre crumbs.

were taken using JSM-IT 100 equipped with JEOL Scanning Electron Microscope (SEM) technologies with Backscattered Electron Composition (BEC) detector manufactured in Tokyo Japan. It was observed that after chemically treating tyre crumbs, there was a development of pores in the sample matrix, which could have provided some boost for the pyrolysis process [24]. This is because heat diffusion could easily be achieved when a material with connected voids was heated. As a result, uniform radiative heat flux could also be obtained. In addition, there was a possibility to obtain a super adiabatic temperature (system) in a porous medium due to the passive preheating of the pyrolysable gases [28,29].

In the case of tyre pyrolysis, pyrolysable gases are fuel gases due to the nature of tyre makeup. For example, some of these fuel gases are compounds from C_1-C_7 and have a boiling or decomposition points of < 20 °C. When these fuel gases are heated up by the reactor, they initiate a reaction meaning that they heat-up other fuel compounds with smaller to medium chains than larger chains, as in a chain reaction. The heat is then accumulated within the tyre matrix until it explodes releasing greater heat or temperature than the reactor provides externally. This propagation of chain reactions, also referred to as self-pyrolysis (i.e when gas, oil, oxidation, and heat transfer takes place simultaneously causing an autocatalytic system resulting in a rapid increase in temperature), is suggested to be taking place in the treated tyre samples.

3.3. Pyrolysis products

3.3.1. Product yield

The results obtained from the experiments conducted are summarised in Table 4 and are categorised based on the amounts of solids, liquids, and gases recovered. The weight percentage of the products was

calculated using mass balance. Sand was used as a baseline in this study to allude the heating rate or the temperature program of the reactor. The Blank (sand) only produced an average of 1,25 % gas and 0 % liquid as expected. Untreated tyre crumb as the reference produced approximately 7 % gas and 1,5 % liquid, which could be attributed to the moisture trapped in the tyre crumbs' matrix. The pre-treated sample had about 49 % solid product, 27 % liquid, and 24 % gas. The oil produced was collected in three (3) separate collectors providing three fractions of oil (Fig. 6; at the temperature range 100–115 °C, 14,5 % out of 27,25 % light oil was produced, then heavier oil poured slowly into the oil collector over time). The oil produced from this experiment had a fuel like odour, with the light oil being reddish in colour and heavier oil black in colour. The (reddish) colour suggests lighter and cleaner oil (C2 and C3), while darker (C1) suggests high heat and contaminants present in the oil (e.g., PAHs). Approximately 53 % of the lighter fraction and 47 % of the heavier fraction were produced from the 27 %.

3.4. Infrared spectroscopy analysis (FTIR) of untreated and treated tyre crumbs before and after 280 °C pyrolysis

Functional groups in the untreated and treated waste tyre crumbs samples before and after pyrolysis at 280 °C were analysed using Attenuated Total Reflectance Fourier-transform infrared (ATR-FTIR). The instrument specifications are as follows: Bruker ATR-single reflection diamond crystal, spectral range: 8000 cm^{-1} – 10 cm^{-1}, FTIR-Bruker Tensor 27. The spectral range used for this study was 4000 cm^{-1} – 400 cm^{-1} with a resolution of 16 and 120 scans. The FTIR spectra in this study appeared skew or sloppy, due to the sample's colour nature; the deeper light penetration at the long-wavelength results in the spectra being slanting or sloping as shown Fig. 7 (A and B). The peaks that can be used to identify NR and SBR in the tyre sample appear at 1372 – 1450 cm^{-1}, which is assignable to the C-H bending vibrations of -CH_2 and -CH_3 in NR, 1600 cm^{-1} assigned to C=C in both 1,4 cis-isoprene (NR) and butadiene (SBR) and lastly 698 – 804 cm^{-1} assigned to mono-substituted benzene in SBR [30,31].

Fig. 7 (A) shows the spectra of untreated tyre crumb before and after pyrolysis at 280 °C. There is no significant difference between the two spectra. The only noticeable change is in the reduction of functional group peak intensities. Fig. 7 (B) shows the spectra of treated tyre crumbs before and after pyrolysis at the same temperature. Due to the chemical pre-treatment new functional groups were observed in the treated tyre crumb sample. The broad peak observed around 3000 – 3400 cm^{-1} was assigned to O-H stretching and the one around 1700 cm^{-1} was assigned to C=O stretching vibration. These functional groups formed during the pre-treatment of the tyre crumbs, confirming that oxidation occurred in the sample. Another broad peak was observed between 1500 – 804 cm^{-1} for the treated tyre crumb. This might have been caused by the distribution of chains due to the broken polymer chain network and/or the effect of new substituted functional groups. The FTIR did not show any functional groups for the treated tyre crumb after pyrolysis. This is because the treated sample after pyrolysis comprises of about 80 wt percent (wt%) of carbon black/char.

3.5. Thermal analysis

3.5.1. Derivative and Thermo-Gravimetric analysis (TGA & DTG)

Thermal analysis of untreated and treated rubber crumb (TGA/DTG analysis) was conducted before and after pyrolysis. Shimadzu DTG-60AH (2014 model) simultaneous DTA-TG instrument was used as a quick technique to monitor the extent of pyrolysis of the untreated and treated tyre crumbs before and after pyrolysis. The conditions used were as follows: 95. 9 % nitrogen gas; gas flow rate 20 mL/min with the following temperature programme: hold at 30 °C for 10 min, then ramp to 800 °C at 50 °C/min and hold for 10 min. Fig. 8 shows thermograms of untreated rubber crumbs before and after pyrolysis, respectively. It can be observed that no significant decomposition took place in the
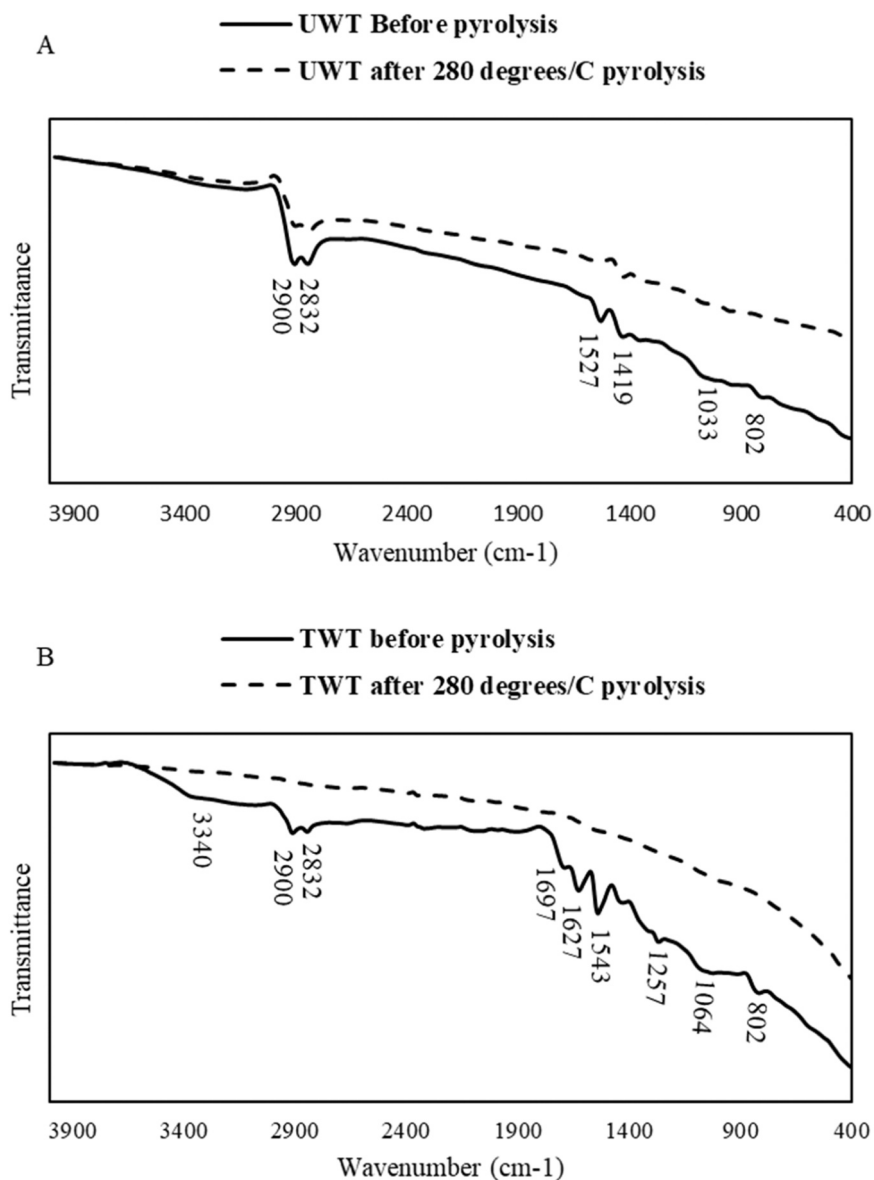
Fig. 7. FITR analysis of tyre crumbs before and after 280 °C pyrolysis. A - untreated tyre crumbs before and after pyrolysis: B - treated tyre crumbs before and after pyrolysis.

untreated rubber crumb, only moisture evaporation took place. This can be seen from DTG graph (orange) that the peaks only reduced in size due to moisture evaporation. This confirms that insignificant, if any, pyrolysis took place as suggested by the pyrolysis temperature program and the yield in Table 3. A sharp drop/event can be seen at about 350 °C; suggesting that it is difficult for pyrolysis to happen below this temperature.

Thermogram of the pre-treated rubber crumb before and after pyrolysis respectively is shown in Fig. 9. Around 100 °C, the pre-treated rubber crumbs start to decompose, and at around 350 °C, about 90 % of the volatile matter has decomposed. The two temperatures (100 °C and 350 °C) were chosen for easy comparison with the pyrolysis temperature program, of which it agreed with the products obtained. However, about 10–13 % pyrolysable/decomposable matter is still present in the rubber crumb matrix exhibiting degradation at around 400–450 °C, which suggests that some polymer was still not completely broken down by the treatment.

Thermal degradation of the samples was studied via TGA analysis. Information obtained was used to study and estimate the extent to which pyrolysis took place. It is well-known that carbon does not decompose

under nitrogen gas. From the untreated thermogram, it can be observed that the carbon black present is about 40 % of the rubber crumb material. From the results presented about 87 % out of 60 % of the pyrolysable matter in rubber crumb (NR and SBR) was pyrolysed. An average of approximately 49 % of the residual remained after pyrolysis. TGA thermogram of the treated rubber crumb after pyrolysis showed that about 10–13 % of the pyrolysable material remained in the residual as the temperatures did not reach the required temperature range (400 – 450 °C) to decompose the material.

3.5.2. Proximate analysis

The proximate analysis provides the weight change of a material with respect to change in temperature. The information obtained from this analysis provides analytical data about the sample's moisture, volatiles/decomposable, fixed carbon, and ash content of the sample. TA Instrument SDT Q600 was used to analyse untreated and treated rubber crumb proximate. The temperature program used in conducting the analysis entailed heating samples from room temperature to 200 °C at a ramp of 50 °C/min. It was kept isothermal at 200 °C for 5 min under nitrogen to measure the moisture content. Samples were then heated
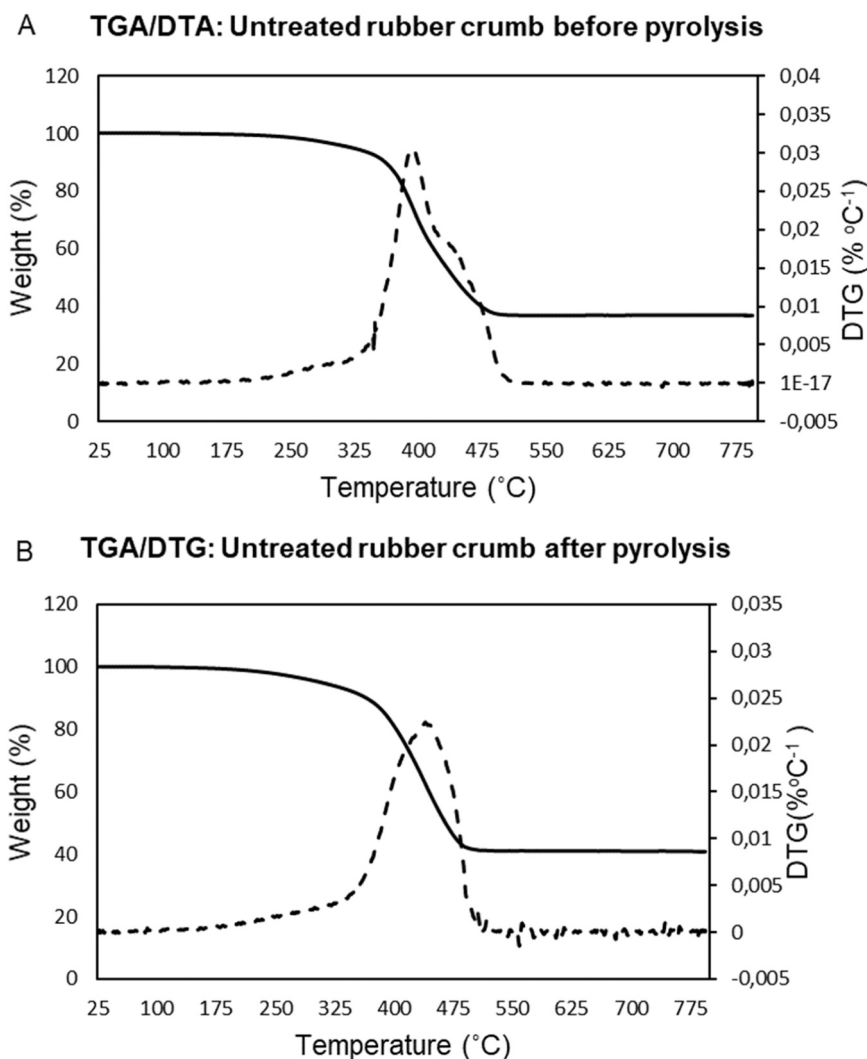
Fig. 8. TGA/DTG thermograms of untreated tyre crumbs before (A) and after (B) pyrolysis.

from 200 °C to 900 °C with a ramp of 50 °C/min under nitrogen and kept isothermal for another 5 min. This was done so that all of the decomposable material in the sample degrade. Since carbon or fixed carbon does not degrade under nitrogen or inert atmosphere, the gas was switched from nitrogen to oxygen at 900 °C, kept isothermal for 10 min to measure the fixed carbon content. The remainder weight was assigned as ash content. Fig. 10 (A and B) shows the proximate thermograms of untreated and treated rubber crumb before and after pyrolysis at 280 °C, respectively.

Another important analysis that could be done using SDT is analysing the heat flow of a sample, since DSC runs simultaneously with TGA. A simple explanation of heat flow is the flowing of energy from one substance to another in a unit time. Heat flow is associated with the release of heat/energy or exothermic reaction/(peak). To measure the heat flow, one can calculate the area under an exothermic peak, or the heat released in J/g of a samples. The heat flow analysis was taken from approximate analysis using TA instrument SDT Q600 with the following temperature program: ambient temperature to 200 °C, ramp at 50 °C/min, hold for 5 min, 200 °C to 900 °C ramp at 50 °C/min and hold for 5 min then switch nitrogen to air and hold for 10 min. This was done to observe and prove the phenomenon taking place at 100 °C in the treated sample. Heat flow of untreated waste tyre (UWT) and treated waste tyre (TWT) before pyrolysis is shown in Fig. 11. It can be observed that at an onset temperature of 100 °C, at 2 min, there is an exothermic reaction with a heat flow of 254.2 J/g in the TWT sample as compared to 27.9 J/

g in the UWT sample. This energy is suggested to be the factor initiating the chain reaction taking place during the explosion of heat.

Table 5 summarises the proximate results obtained from untreated and treated rubber crumbs before and after pyrolysis at 280 °C. It can be seen from the proximate results that the are no significant changes between untreated rubber crumb samples before and after pyrolysis (can also be seen in Fig. 10A). This is because major decomposable materials in a tyre composition do not undergo pyrolysis at 280 °C. As mentioned under results and discussion, NR and SBR degrade at 300 – 450 °C. The process oil used in manufacturing tyre process degrades around 200 – 250 °C, hence there is a slight difference in the weight percentage in the moisture and decomposable.

Before pyrolysis, the treated rubber crumb (Fig. 10B) shows a significant change compared to untreated rubber crumb before pyrolysis. As per the objectives of this study, it shows that the tyre chain network was successfully broken into smaller chains and about 18.5 % degraded at 200 °C with the major pyrolysable material at 39.8 %. Looking at the proximate percentages one may expect only 18.5 % to be pyrolysed at 280 °C in the treated rubber crumb as the polymer content degrades at 300 – 405 °C. Due to the self-pyrolysis phenomenon in the pyrolysis system, the temperature increased to about 334 °C and further degraded part of the polymer material. Only about 12 % of decomposable/polymer were left, and about 79 % fixed carbon was present in the sample.
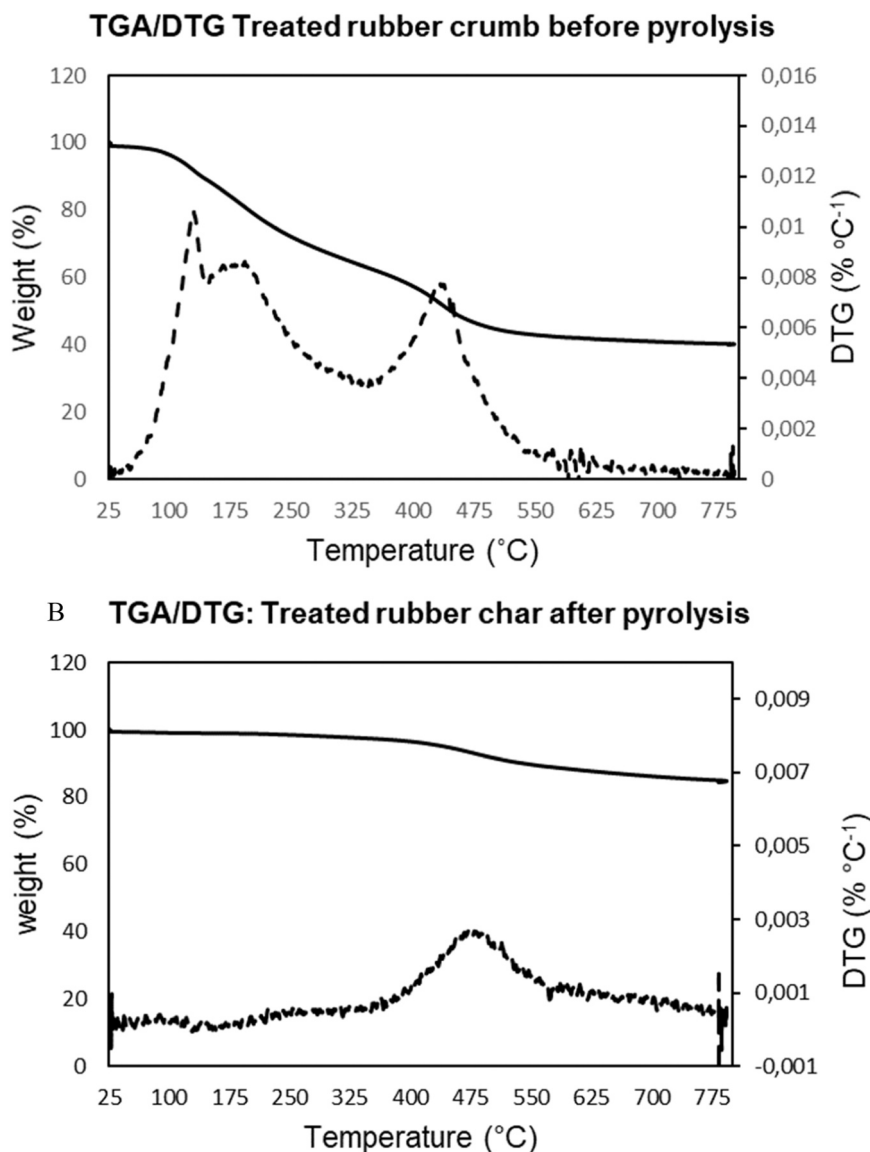
TGA/DTG Treated rubber crumb before pyrolysis

B TGA/DTG: Treated rubber char after pyrolysis

Fig. 9. TGA/DTG thermograms of treated tyre crumbs before (A) and after (B) pyrolysis.

3.6. Elemental analysis (CHNS)

Elemental analysis was performed using Thermo-Scientific Flash 2000 coupled to LC premier micro-mass spectrometer. This analysis was used to help understand the distribution of carbon, hydrogen, nitrogen, sulphur, and oxygen (CHNS/O) in the treated and untreated waste tyre samples. The instrument was set to record only the CHNS, and the O was estimated by the difference of the total (O % = 100 % - (C+H+N+S) %). The summarised results obtained from the elemental analysis are recorded in Table 6. The hypothesis is that carbon has been drastically reduced from 80.6 % - untreated waste tyre crumb (UWT) to 57.2 % - treated waste tyre crumbs (TWT) before pyrolysis, due to the chemical treatment. Therefore, it is suggested that some of the carbon atoms may have been released in gas form during the chemical reaction. An increase in oxygen atoms is also observed in the treated waste tyre crumbs. This verifies the conjecture that some polymer backbones chains were broken as postulated. Furthermore, studies have shown that acids have the ability to oxidise vulcanised polymer depending on the severity of the conditions hence the increase in oxygen on the elemental analysis after chemical treatment [32,33].

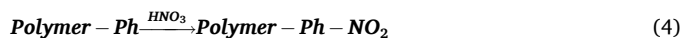The oxidation taking place in TWT sample was suggested to follow the oxidization mechanism of vulcanised polymer using nitric acids [32–36]. Savige et al. [34], investigated the effect of disulphide groups in the presence of nitric acid in a controlled system form hydrogen sulphide as shown in Eq. 2.

$$R-S-S-R \xrightarrow[HNO_3]{Oxidation} R-SO_3H \tag{2}$$
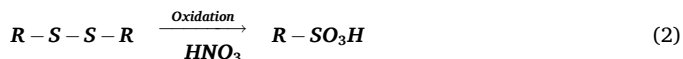
The study further showed that under aggressive conditions the sulfonic groups continues to oxidise forming sulphate and released to the aqueous phase as shown in Eq. 3.

$$R-SO_3H \xrightarrow[HNO_3]{Oxidation} SO_4^{2-} \tag{3}$$

Eq. 4 shows a known reaction mechanism of nitration reaction of styrene polymer process with HNO_3 [35,36].

$$Polymer-Ph \xrightarrow{HNO_3} Polymer-Ph-NO_2 \tag{4}$$

A **Proximate analysis of untreated rubber crumb before and after 280°C pyrolysis**

B **Proximate analysis of treated rubber crumb before and after 280°C pyrolysis**
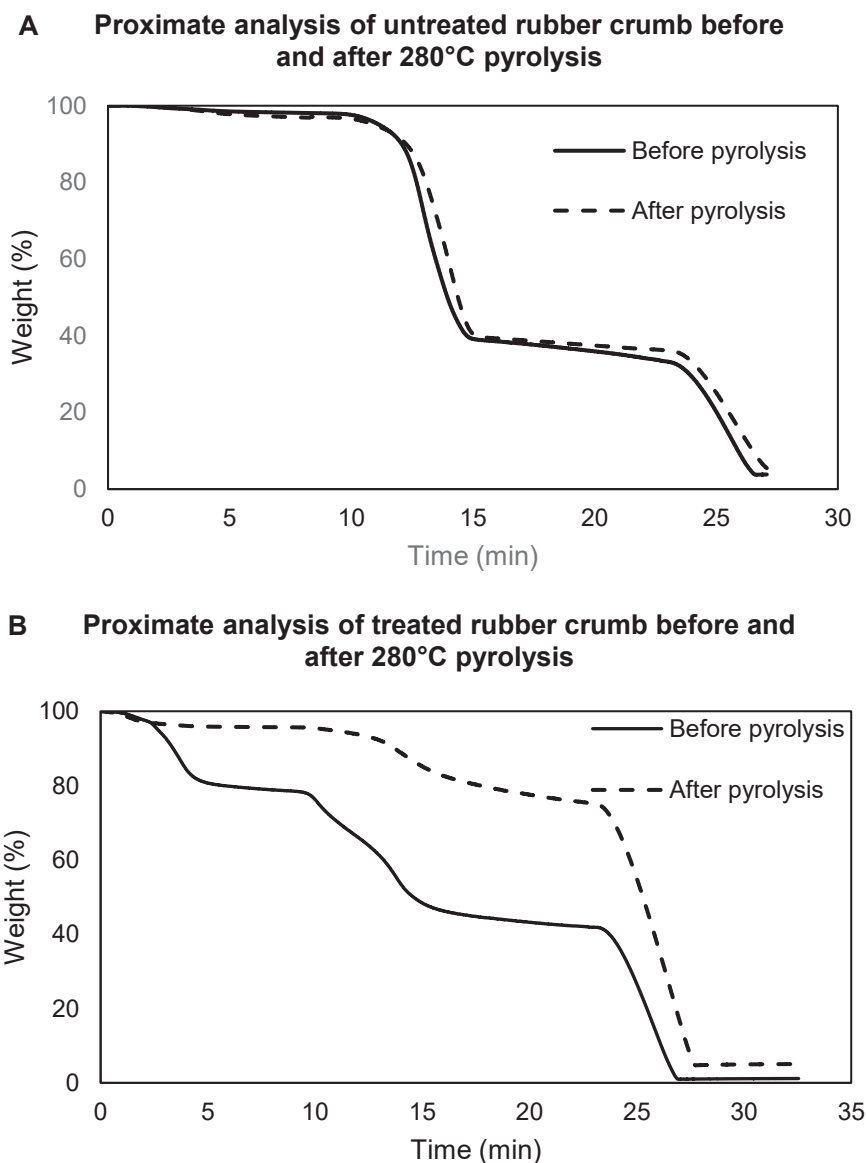

Fig. 10. Proximate analysis thermograms of untreated tyre crumbs before and after pyrolysis (A) and treated tyre crumbs before and after pyrolysis (B).

3.7. Characterization of tyre derived oil produced from chemical pre-treated waste tyres

3.7.1. Infrared spectroscopy analysis (FTIR) of treated waste tyre derived oil after 280 °C

Functional groups from treated TDO were analysed using Attenuated Total Reflectance Fourier-transform infrared. The instrument specifications were as follows: Bruker ATR-single reflection diamond crystal, spectral range: 8000 cm^{-1}-10 cm^{-1}, FTIR Bruker Tensor 27. The spectral range used in this study was 4000 cm^{-1} – 400 cm^{-1} with a resolution of 16 and 120 scans. The spectra of treated TDO produced from the three collectors after 280 °C pyrolysis is shown in Fig. 12. The following functional groups were assigned to the following peaks: 3000–3400 cm^{-1} is assigned to -OH, 2800–2900 cm^{-1} to -CH stretch, 1700 cm-1 to C=O, 1600 cm^{-1} to C=C, 1374–1450 cm^{-1} -CH2 and CH3, 1000–1260 cm-1 to phenols, and 804–900 cm^{-1} to mono-substituted benzene. TWT collector 2 (C2) possesses -OH functional groups which can be seen at wavenumber between 3400 – 3000 cm^{-1} and phenol peak at 1000 – 1260 cm^{-1}. This also shows that the oil is oxidized.

3.7.2. Chromatography analysis of treated waste tyre derived oil

3.7.2.1. Gas chromatography coupled to mass spectrometer analysis. The GC-MS method for treated waste tyre derived oil was developed by optimization of temperature programme for better separation in the column. The samples were not diluted but the split ratio was increased to 70:0 and the injection volume was 0.1 μL. Due to the complexity of tyre composition, the resulting TDO was even more complex and therefore difficult to calibrate each detected peak. The detected peaks were classified in groups that the study was focusing on, which are contaminants group (sulphur and PAHs compounds) and positive compounds that could be further utilized (alkanes, alkenes (only low molecular weight alkenes were calculated and displayed on the graph due to their market value e.g., terpenes), acids which were facilitated by the presence of oxygen in the treated sample and BTX). The identity of these compounds are shown in Table S2, under sub-heading SM-3 and m/Z spectra of the compounds of interest. These compounds were grouped into their respective fractions from the collectors (C1, C2, and C3). Fig. 13 display the relative area percentages of different groups of compounds. It was observed that in C1 collector there was high sulphur and PAHs percentages compared to C2 and C3. This is because C1 collector has the
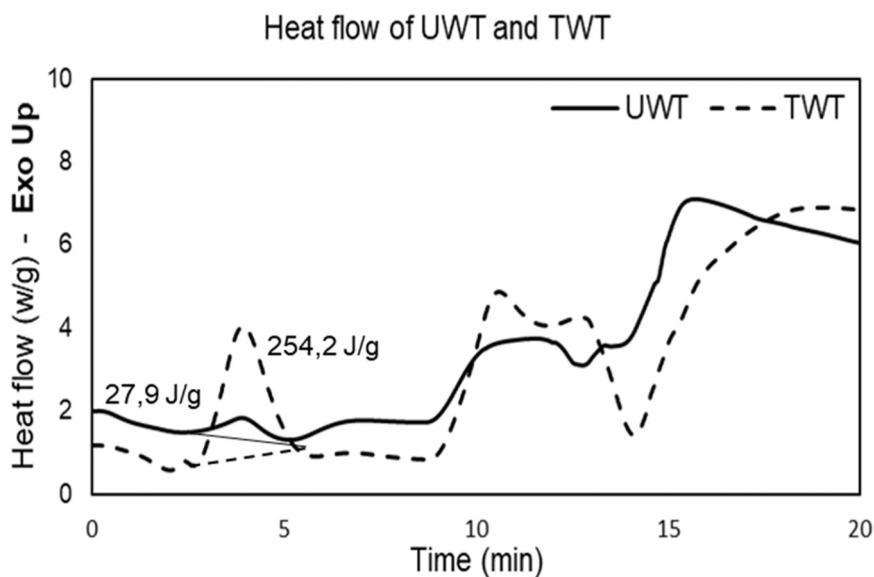
Fig. 11. Heat flow thermogram of UWT and TWT samples before pyrolysis.

coupled to a selective sulphur detector. Eq. 5 was used to calculate the sulphur content in each of the collectors.

$$[S]_t = \sum gA_t = gA_i = \frac{[S]_o}{[S]_t} = \frac{[A]_o}{[A]_t} \tag{5}$$

It can be seen from Table 7 that C-1 had the highest sulphur content compared to C-3 and C-2, respectively.

In literature, TDO is typically recorded to have a high sulphur content of about 1.0 – 1.4 wt%, which is caused by the vulcanizing agents used in the tyre formulation [37]. It is suggested that chemical pre-treatment of the waste tyre caused breakage of some of the sulphur-sulphur and sulphur-carbon bonds which affected the sulphur content in the oil. In addition, the sulphur content of UWT TDO was documented in previous study of the oil produced from UWT versus TWT [23]. One of the observations made during the pre-treatment process of waste tyres was a yellowish-brown gas emission, which was suspected to contain some of the sulphurous gases due to elemental analysis showing a decrease in the sulphur content after treatment. Fig. 14 shows a picture of chemical treatment setup with the yellowish-brown gas visible/showing in the Erlenmeyer flask. Some of the sulphur compounds were allocated to as H_2S and SOx gasses that may have evaporated during pyrolysis process.

4. Conclusions

This study aimed to find an alternative way of reducing the typical tyre pyrolysis temperature from a minimum of 400 °C to a minimum of 280 °C. This was achieved by chemical pre-treatment of the waste tyre crumbs under ambient conditions. It was hypothesised that this chemical pre-treatment breaks down the polymer backbone to acquire low molecular weight chains, requiring less energy to pyrolyse waste tyres. The temperature explosion or spike from 100 – 334 °C was observed during pyrolysis of treated waste tyre which cause propagation of chain reaction resulting in self-pyrolysis in the system. This meant that at the initial pyrolysis temperature in this case 100 °C, the external source of temperature may/can be switch off and the system will self-sustain.

This study demonstrated the effectiveness of pre-pyrolysis treatment using acid-solvent mixture to pyrolyse waste tyres at significantly low temperatures. In addition, the resultant products showed low sulphur content and low PAHs. This translates to significantly lower energy costs and bearable odour.
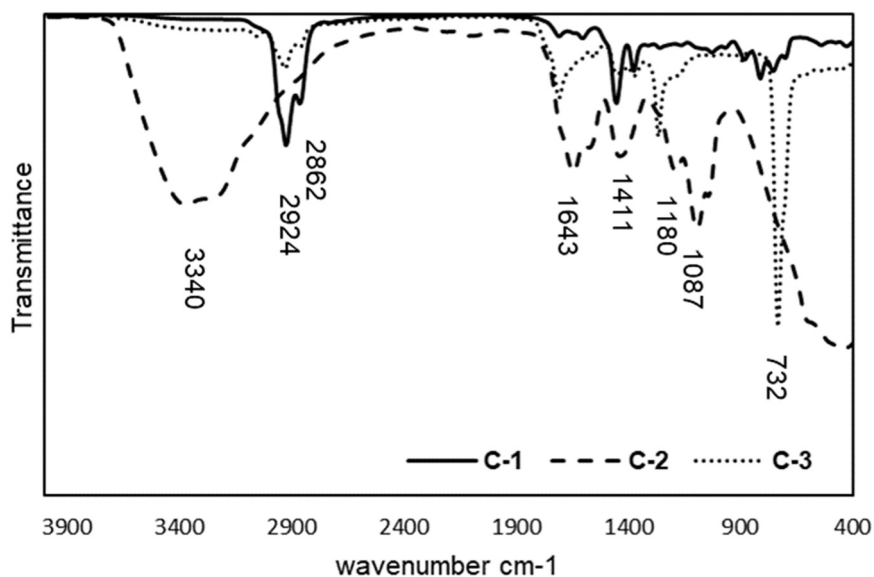
Table 5
Summarised proximate results for untreated and treated tyre crumbs before and after pyrolysis.

Untreated rubber crumb				
	(wt%)			
	Moisture	Volatiles	Fixed carbon	Ash
Before pyrolysis	2.29	57.75	35.98	3.98
After pyrolysis at 280°C	3.46	56.51	34.62	5.12
Treated rubber crumb				
Before pyrolysis	18.46	39.82	40.56	1.17
After pyrolysis at 280°C	3.97	11.65	79.32	5.07

Table 6
Summarised elementals analysis results of untreated and treated waste tyres before and after 280 °C pyrolysis.

Component name	Element percentage (%)			
	UWT - Before	UWT - After	TWT - Before	TWT - After
Nitrogen	0.42	0.40	6.54	4.22
Carbon	80.62	81.63	57.23	75.60
Hydrogen	7.46	7.03	4.72	2.82
Sulphur	1.76	1.85	1.13	0.84
Oxygen	9.74	9.09	30.19	16.52

heaviest fraction from the three collectors. C2 collector had the highest acids and alkanes in comparison to the other collectors while C3 had the highest BTX compounds.

3.7.2.2. Gas chromatography coupled to flame photometer detector analysis. Gas chromatography coupled with flame photometer detector (FPD) is one of the common instruments used in sulphur and phosphorous analysis. The FPD detector operates as follows: sulphur compounds from the GC column are burnt in a hydrogen-rich flame to produce S_2 which emits radiation near 400 nm. This radiation is monitored by a photomultiplier tube. Shimadzu GC-FPD instrument was used with the following column specification: Zeblon ZB-1: 30 m, 0.25 mm, 0.25 µm. GC-FPD analysis for sulphur content in the TDO produced was conducted following the ASTM D5623 standard method. ASTM D5623 is a standard test method for determining/verifying the sulphur-containing compounds in light petroleum liquids using gas chromatography

Fig. 12. FTIR spectra of the chemical treated waste tyre derived oil in their respective collectors (C1, C2 and C3).
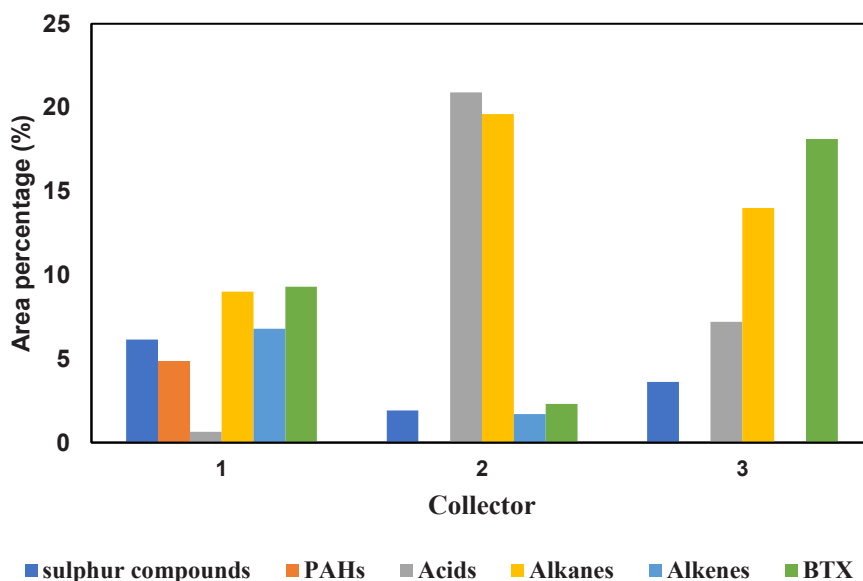

Fig. 13. Classifications of GCMS compounds from TWT oil in their respective collectors.

Table 7
Sulphur content calculated for TWT TDO in different collectors.

	TWT TDO (ppm)
Collector 1	1634.4
Collector 2	128.2
Collector 3	460.4
Total sulphur content (ppm)	2223
Total sulphur content (wt%)	0.22

Author contributions

P.C.T. and S.P.H conceived the research; P.C.T. performed the experiments; P.C.T., M.M.P., S.A.I., N.M.M., M.J.P., and S.P.H. analysed the data, discussed the results, and drew the conclusions; P.C.T wrote the original manuscript draft; M.M.P., S.A.I., N.M.M., M.J.P. and S.P.H. review and edited the manuscript; Supervision, S.A.I., N.M.M. and S.P. H.

CRediT authorship contribution statement

Samuel Ayodele Iwarere: Formal analysis, Investigation, Methodology, Supervision, Writing – review & editing. **Shanganyane Percy Hlangothi:** Writing – review & editing, Supervision, Formal analysis, Conceptualization. **Mohau Justice Phiri:** Writing – review & editing, Formal analysis. **Malusi Ntandoyenkosi Mkhize:** Writing – review & editing, Supervision, Formal analysis. **Mapoloko Mpho Phiri:** Writing – review & editing, Formal analysis. **Phuti Cedrick Tsipa:** Methodology, Formal analysis, Writing – review & editing, Conceptualization, Writing – original draft.

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.

Fig. 14. Pictorial image of tyre crumb pre-treatment showing the yellowish-brown gas emitted during the process.

Data Availability

No data was used for the research described in the article.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2024.106631.

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