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Co-combustion of tyre waste char and biomass blends using thermogravimetric-mass spectrometric analysis

Tyre waste chars from pyrolysis are a potential fuel source due to their attractive energy properties and high carbon content. However, the high concentration of sulfur in tyre char and the release of carbon dioxide (CO_2) when burned prevent its use as a fuel. In this study, *Scenedesmus* microalgae and torrefied pine wood waste were blended with tyre waste chars. Blending was done at varying biomass ratios. The aim was to evaluate the effects of biomass additions on tyre char combustion characteristics and gas emission resultants using the thermogravimetry-mass spectrometry method. Results show that the combination of biomass with tyre char significantly affects the physicochemical properties of the tyre char. Biomass enhances the combustion characteristics of tyre char. Ternary blends with optimised proportions of microalgae led to higher burnout temperatures and prolonged combustion phases. Torrefied wood–tyre char blends at a 90:10 ratio showed higher rates of CO_2 evolution, but adding torrefied wood at 15–20 wt% and increasing microalgae from 4 to 11 wt% reduced CO_2 emissions. The experimental results show that tyre char could be a potential combustion co-fuel with biomass feedstock and suitable for clean combustion applications. The study emphasises the critical role of incorporating clean, renewable biomass sources in mitigating gas emissions during the combustion of tyre waste chars, thereby promoting the sustainable utilisation of carbon resources. Additionally, the integration of biomass to enhance the usability of tyre waste chars presents a promising opportunity to improve the economic viability of the waste tyre pyrolysis process.

Significance:

Tyre char is a waste by-product from the pyrolysis of waste tyres. It possesses good energy properties and can be used as a fuel, but its combustion is undesirable due to the generation of carbon dioxide during combustion. The blending of tyre char with biomass material influences the physicochemical properties of tyre char and can have a consequent effect on the combustion characteristics of these chars. The addition of microalgae and torrefied wood at various blending ratios had a significant influence on the reduction of CO_2 emission patterns in the tyre char–biomass blends. Tyre char–biomass blends can be considered for cleaner combustion processes.

Introduction

The by-product of waste tyre pyrolysis is known as tyre pyrolysis char and presents an inescapable environmental challenge due to its detrimental impact on both health and the environment if left unattended after the tyre pyrolysis process.[1] Consequently, there has been a growing need to explore viable methods for repurposing these pyrolytic chars, promoting environmental sustainability and enhancing the economic viability of the waste tyre pyrolysis process.[1,2] The focus of many studies has been on recycling and upgrading waste tyres to create products that can replace commercially available carbon black.[1,2] In addition, researchers have explored thermal treatments for tyre chars to remove impurities and enhance their physicochemical properties, thereby elevating their potential as substitutes for carbon black in high-value applications.[1]

Tyre chars are also considered a viable option for energy production as they can serve as a solid fuel source for heat and energy generation in various industries, including cement factories.[3-5] The potential utilisation of tyre pyrolysis char for fuel purposes is attributed to its high calorific value and carbon content, as well as its chemical composition that is comparable to coal chars.[3,6] However, the practical use of tyre pyrolysis chars as a combustion fuel has been hindered by a combustion process characterised by extended residence times at high temperatures and the generation of large amounts of carbon dioxide (CO_2).[6,7]

Additionally, the tyre chars contain significant levels of retained sulfur (2 wt%) and heavy metals that could be released during combustion.[1,7,8] An effective strategy to overcome the limitations that prevent the utilisation of tyre chars as a fuel feedstock is the blending and co-firing of tyre char with environmentally friendly and carbon-neutral bio-renewable resources, such as aquatic and woody biomass. This approach offers several advantages, including the elimination of the need for extensive treatment or purification processes, such as leaching or thermal treatment, to produce activated carbons from tyre char.[1,7,8] Aquatic biomass, including microalgae biomass, has been successfully used in the blending and co-combustion of solid fuels such as coal.[9] Microalgae offer an attractive feature in fuel blending by reducing the ash and sulfur content by enhancing the combustion characteristics of the fuel mixture.[10-12]

Another promising feedstock for co-combustion with waste tyre char is torrefied biomass. Torrefaction significantly reduces the moisture content in biomass materials, whether they are of woody or herbaceous origin. This reduction in moisture content limits biological activity (such as rotting), leading to improved shelf life and higher energy density. As a result, torrefied biomass exhibits higher calorific values compared to raw biomass.[13,14] The co-processing of waste tyre chars with renewable biomass offers a promising solution to address environmental

and energy challenges. This innovative approach not only reduces the reliance on fossil fuels but also mitigates the waste disposal issues associated with tyre pyrolysis by-products, specifically waste tyre char. The integration of these materials can significantly enhance waste tyre management, improve the economic viability of tyre utilisation and tap into the energy potential of biomass sources.

In several studies, various researchers investigated the combustion characteristics of solid fuels and biomass combinations using thermogravimetric analysis. Xinjie et al.[15] found that adding biomass to high-volatile bituminous coal increased reactivity during combustion, especially compared to low-volatile anthracite coal. Magida et al.[11] explored coal–microalgae blends and observed that higher microalgae ratios lowered ignition and burnout temperatures, resulting in reduced emissions of CO_2, NO_2, SO_2 gases and oxides of nitrogen (NO_x). Ye et al.[9] noted that microalgae enhanced coal combustion by providing additional heat. Ejesieme et al.[12] observed interactions among different fuels, with coal–microalgae and coal–charcoal blends showing synergistic behaviour.

Mundike et al.[16] found that blending plant char with coal decreased burnout temperatures and improved coal combustion. Jayaraman et al.[17] studied coal–biomass blends and reported increased reactivity and lower burnout temperatures with higher biomass ratios. In a recent study by Qiao et al.[6] that focused on the combustion characteristics of tyre chars and changes in combustion products in comparison to various coal types, it was found that tyre char can be a potential substitute fuel for coal coke and semicoke because of its reactivity and high calorific values. Slyusarasky et al.[18] analysed the co-combustion characteristics of tyre char/peat and tyre char/pine sawdust. Their findings showed that biomass additions to maximum loadings (15 wt%) could enhance the reactivity of the chars and significantly decrease the ignition delay times at heating medium temperature in a combustion chamber. Also, the use of biomass as an additive could substantially reduce the emission of sulfur dioxide. The literature findings highlight the positive impact of biomass on solid fuel combustion and emphasise the need for further research on the blending effects of biomass on tyre pyrolysis char.

To our knowledge, no prior study has investigated the co-effects of aquatic and ligneous biomass on the combustion characteristics of tyre waste chars. This study explores the use of microalgal and torrefied biomass as additives to tyre chars to form fuel blends. In this study, *Scenedesmus* microalgae and torrefied pine wood waste were blended with tyre waste chars. Blending was done at varying biomass ratios. Thus, the objectives were to (1) prepare different formulations (fuel blends) of char and biomass and characterise these and the raw samples for their physicochemical properties, to study the effects of biomass ratio on the physicochemical properties of tyre waste char and (2) carry out the combustion tests on the raw and blended samples using a thermogravimetry-mass spectrometry, to study the combustion behaviour of the blended samples. The aim of this study was therefore to evaluate the effects of biomass additions on tyre char combustion characteristics and gas emission resultants using the thermogravimetry-mass spectrometry method. The high sulfur content in tyre char and the release of CO_2 during combustion limit its viability as a fuel source. Co-combustion with clean, renewable biomass sources is intended to enhance the combustion characteristics of the char while contributing to the reduction of gas emissions.

Experimental

Origin and preparation of samples

A fine granular tyre char sample (250 μm) was obtained from a South African company. A representative sample of the char was pulverised on a Keegor vertical spindle pulveriser to a particle size of sub-250 μm and sieved to obtain a sub-150 μm sample that was stored in an airtight container. Pinewood waste (purchased from a local store in Gqeberha, South Africa) was torrefied in a fixed bed reactor at 320 °C, at atmospheric pressure, in an inert environment at a constant flow rate of 400 mL/min. A representative sample of torrefied wood was prepared in the same manner as the tyre char. A microalgae *Scenedesmus* sp. sample was obtained from the Institute of Chemical Technology (InnoVenton). The microalgae were cultivated in the integrated vertical column photo-bioreactor-raceway cultivation system. The microalgae

were then harvested and concentrated through sedimentation as reported by Gaqa and Watts[10]. The biomass was harvested by concentrating the microalgae slurry in the growth medium using natural settling in a settling pond overnight and returning the top layer of the growth medium to the cultivation system. Thereafter, the concentration of microalgae (on a dry weight basis) was determined as the mass of dry microalgae in grams per gram of slurry harvested.

Microalgae slurry was used for the blending experiments with tyre char and torrefied wood. However, for analysis purposes, the microalgae slurry was lyophilised in a Vacutec freeze drier connected to a 2XZ-2 rotary vane vacuum pump for at least 72 h until the sample had reached 25 °C. The freeze-dried sample was then crushed into flakes using a mortar and pestle and stored in an airtight container. A total of 14 mixtures, including four duplicates, were prepared using a D-optimal mixture design. The lower and upper limits for the mixture design were as follows: tyre char 55–90 wt%; torrefied wood 10–30 wt% and microalgae 0–15 wt%. These limit ranges were selected to ensure that the tyre char was the main feedstock in the blend and to ascertain that only the minimum required amounts of torrefied wood and microalgae were used, to be able to study their effects on the combustion characteristics of the tyre char. The tyre char and torrefied wood blends were homogenised using a mixing rod and continuously stirred in a container, whereas the mixtures of tyre char, torrefied wood and microalgae slurry were stirred continuously at 100 rpm using a Heidolph RZR 2041 stirrer and centrifuged using HEMLE Z-383 (Lasec SA) at 4500 rpm, for 15 min to ensure that the microalgae slurry was well mixed with the tyre char and torrefied wood. The ternary mixtures were oven dried overnight at 105 °C. The dried samples were then ground with a mortar and pestle. All mixtures were screened and sieved to a sub-150 μm particle size and stored in an airtight container.

Characterisation of parent fuels and char–biomass blends

All samples were analysed for physical and chemical properties. The proximate analysis was conducted according to the ASTM 7582 standard methods (using an ELTRA Thermostep macro TGA). The ELTRA Thermostep TGA has an integrated programmable furnace, weighing balance and heating program. It performs an automated proximate analysis that determines the weight percentages (wt%) of the volatile matter content at 900±20 °C for 7 min and the ash content at 750 °C for 2 h, which is preceded by the moisture analysis at 105±2 °C for 1 h. The fixed carbon is then calculated by difference. For each analysis, 1 g of sample was weighed and analysed. The ultimate analysis was conducted to determine the percentages of weight (wt%) of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) according to ASTM D3176 using the Vario EL Cube. The elemental content was determined by combusting 5 mg of the sample at 1150 °C. The calorific values of the raw and mixed samples were measured with a LECO AC 600 bomb calorimeter using the TruSpeed® method (ASTM D5865). The PANalytical Epsilon 3 X-ray fluorescence instrument was used for the identification and quantification of inorganic elements present in all samples (5 g of each sample). Micromeritics Instrument Corporation (TriStar II 3020) analyser was used to determine the surface areas of the parent samples using N_2 adsorption.

Thermogravimetric analyses

Thermogravimetric analysis of the samples was performed using the TGA 5500 Discovery series coupled with a bench-top quadruple mass spectrometer. About 5 mg of the powdered sample was contained in platinum plates and subjected to combustion under air. The sample was heated at 10 °C/min from ambient to 650 °C, and the airflow rate was maintained at 50 mL/min.

Results and discussion

Physicochemical properties of the parent fuels and char blends

The results of the proximate and ultimate analysis of the parent fuels and the blended char–biomass samples are shown in Table 1. The results show the average values and uncertainty (+/−) values at a 95%

Table 1: Physicochemical properties of the raw and blended char samples

| Sample	Sample ID	Proximate analysis (wt%wt%, dry basis)			Ultimate analysis (wt%wt%, dry, ash-free)					Gross calorific value (MJ/kg)
		Volatile matter	Ash	Fixed carbon	C	H	N	S	O	
Tyre char	TC	11.1 ± 0.5	16.5 ± 0.3	72.4 ± 0.7	90.7 ± 1.5	1.2 ± 0.7	0.2 ± 0.7	3.5 ± 0.1	4.4 ± 1.3	25.8 ± 0.2
Torrefied wood	TW	41.1 ± 0.9	2.5 ± 0.0	56.4 ± 0.9	76.0 ± 0.6	4.5 ± 0.4	0.1 ± 0.0	0.5 ± 0.6	18.9 ± 0.0	27.5 ± 0.1
Microalgae	M	75.4 ± 0.2	11.8 ± 0.9	12.8 ± 0.7	57.7 ± 0.9	8.7 ± 0.6	10.5 ± 0.6	0.8 ± 0.0	22.2 ± 0.4	22.2 ± 0.2
1	TC55-TW30-M15a	20.4 ± 0.6	11.1 ± 0.7	68.5 ± 0.4	81.9 ± 0.2	2.1 ± 0.7	1.9 ± 0.7	1.2 ± 0.2	12.9 ± 1.5	26.1 ± 0.1
2	TC55-TW30-M15b	19.9 ± 0.4	11.3 ± 0.1	68.8 ± 0.4	81.7 ± 0.7	2.3 ± 0.5	2.0 ± 0.2	1.2 ± 0.1	12.8 ± 0.9	26.5 ± 0.1
3	TC62-TW30-M8	21.2 ± 0.9	11.2 ± 0.7	67.6 ± 1.5	86.8 ± 0.7	2.1 ± 0.2	0.9 ± 0.3	1.6 ± 0.1	8.6 ± 0.5	26.6 ± 0.0
4	TC65-TW20-M15	24.5 ± 0.7	11.4 ± 0.2	64.1 ± 0.4	85.3 ± 1.3	2.4 ± 0.1	2.0 ± 0.2	1.7 ± 0.1	8.6 ± 1.6	25.9 ± 0.1
5	TC70-TW30-M0a	20.3 ± 0.6	12.3 ± 0.3	67.4 ± 0.3	85.6 ± 0.5	1.7 ± 0.1	0.1 ± 0.2	2.4 ± 0.1	10.2 ± 0.3	26.5 ± 0.0
6	TC70-TW30-M0b	20.2 ± 0.4	12.0 ± 0.5	67.8 ± 0.8	83.4 ± 0.9	2.3 ± 0.2	0.1 ± 0.2	2.2 ± 0.0	12.0 ± 1.5	26.2 ± 0.0
7	TC72-TW20-M8	18.0 ± 0.2	11.5 ± 0.6	70.5 ± 0.7	84.2 ± 0.5	1.8 ± 0.4	0.9 ± 0.1	1.9 ± 0.0	11.2 ± 0.8	26.2 ± 0.1
8	TC74-TW15-M11	19.7 ± 0.3	11.8 ± 0.6	68.5 ± 0.7	85.6 ± 0.5	1.8 ± 0.2	1.5 ± 0.2	1.9 ± 0.1	9.2 ± 0.7	26.2 ± 0.1
9	TC75-TW10-M15a	21.1 ± 0.4	11.9 ± 0.7	67.0 ± 0.5	84.8 ± 0.4	2.2 ± 0.4	1.6 ± 0.3	1.8 ± 0.3	9.6 ± 0.6	26.6 ± 0.1
10	TC75-TW10-M15b	21.7 ± 0.5	12.3 ± 0.2	66.0 ± 0.61	84.0 ± 0.4	1.9 ± 0.9	1.8 ± 0.1	1.8 ± 0.3	10.5 ± 1.2	26.7 ± 0.2
11	TC81-TW15-M4	17.4 ± 0.4	13.7 ± 0.3	68.9 ± 0.64	85.3 ± 1.1	1.3 ± 0.1	0.1 ± 0.1	2.3 ± 0.4	11.0 ± 1.5	26.3 ± 0.1
12	TC82-TW10-M8	19.5 ± 0.6	14.2 ± 0.3	66.3 ± 0.7	87.4 ± 0.7	2.3 ± 0.1	0.2 ± 0.1	2.3 ± 0.1	7.8 ± 0.7	26.7 ± 0.1
13	TC90-TW10-M0a	15.5 ± 0.4	13.7 ± 0.0	70.8 ± 0.4	86.3 ± 0.4	1.9 ± 0.4	0.7 ± 0.2	2.8 ± 0.9	8.3 ± 0.3	26.2 ± 0.1
14	TC90-TW10-M0b	13.9 ± 0.5	15.6 ± 0.1	70.5 ± 0.4	88.6 ± 0.8	1.4 ± 0.3	0.1 ± 0.1	3.2 ± 0.1	6.6 ± 0.9	25.8 ± 0.1

confidence interval. The fixed carbon and oxygen were calculated by difference. The proximate analysis results revealed that tyre char is characterised by a low volatile matter content. However, the addition of high volatile biomass contributed to the marked increase in the volatile matter content of the resulting mixtures (ranging from 13.9 wt% to 24.5 wt%) as biomass loadings increased. Furthermore, the addition of high-energy biomass resulted in a marginal improvement in the calorific values of the blends. Ultimate analysis results show that the tyre char exhibited the highest sulfur content at 3.5 wt%. This elevated sulfur content can be attributed to the presence of thermally stable sulfur-containing compounds, such as zinc sulfide (ZnS) and iron sulfide (FeS), which persist in the char after the pyrolysis process.[8] The combustion of materials with high sulfur content is associated with the release of various sulfur compounds, making the fuel undesirable.[19] In particular, the incorporation of biomass in the blends appears to reduce the sulfur content (to up to 1.2 wt%), as evidenced by the lower sulfur levels in the ternary blends compared to the tyre char. It is worth highlighting that the biomass of microalgae contains a substantial amount of hydrogen, specifically 8.7 wt%. Consequently, char–biomass blends that exhibit significant microalgae concentrations (8 wt% and 15 wt%) exhibit a notable enhancement in hydrogen content compared to the original tyre chars. This increase in hydrogen content has the potential to improve the combustibility of the blended fuel material.[10] X-ray fluorescence results of the composite materials indicated that the binary mixtures and certain ternary mixtures exhibited significant concentrations of calcium, approaching the levels found in the original tyre char. Calcium plays a catalytic role in the combustion process.[20] At elevated temperatures, calcium can be released as volatile emissions and calcium oxide serves to sequester sulfur, resulting in reduced sulfur emissions during combustion.[21] The highest amounts of silicon were detected in ternary blends (blends 1 and 2); these blends contain high amounts of biomass. Silicon, recognised for its thermal stability during combustion, is essential for minimising the accumulation of ash deposits.[22] Zinc was found to be the predominant metal present in tyre char and maintained relatively high levels, even after the addition of biomass, except for the ternary blends (blends 1 and 2), where a notable decrease in zinc was observed. Typically, tyre chars generated via tyre pyrolysis tend to preserve significant levels of zinc, which exist in the compounds of zinc sulfide.[6] The Brunauer-Emmett-Teller surface area measurements showed that tyre char was found to be much larger than that of the microalgae biomass and the torrefied wood samples (Figure 1). The surface area measurements were as follows: 49.7 m²/g (tyre char), 1.6 m²/g (torrefied wood) and 21.3 m²/g (microalgae). No further analysis was done on the blended samples. Therefore, it is not expected that any addition of biomass material within the lower and upper limits of the set could have any impact on the surface area of the tyre char.

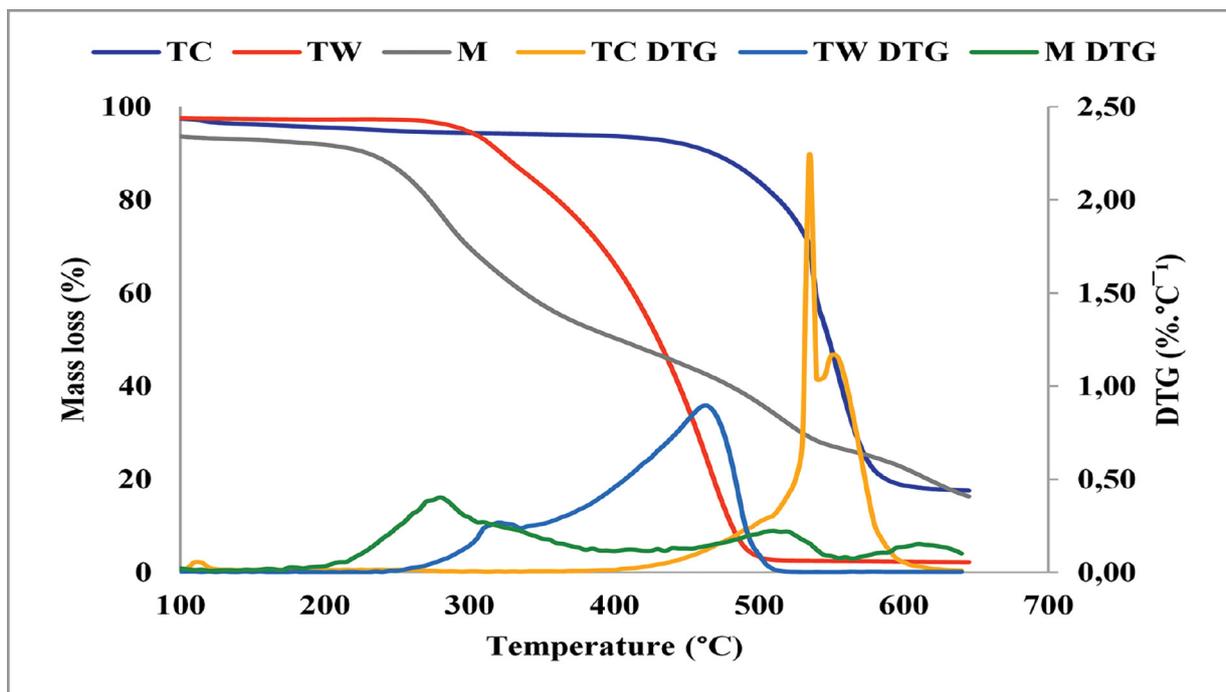### *Thermogravimetric analysis*

Thermogravimetric mass loss and derivative thermogravimetric curves of the individual fuels are shown in Figure 2. The combustion characteristics (the initial decomposition temperature, derivative thermogravimetric maximum of each peak, as well as the char ignition and burn-out temperatures) of the raw and blended samples are listed in Table 2. Figure 2 shows the thermal events associated with microalgae combustion. These events exhibit distinct characteristics. The first significant event is the volatile combustion event between 150 °C and 350 °C. During this phase, inherent lipids, carbohydrates and proteins in microalgae are decomposed, and the production of char occurs.[23,24] Another thermal event occurs between 450 °C and 550 °C, attributed to the breakdown of lipids. This phase is marked by the disintegration of hydrocarbon fatty acids.[25] The reactivity of the primary combustion events in microalgae diminishes with increasing temperature because of the depletion of compounds with low thermal stability, such as volatile components, at lower temperatures.[24]

The decomposition of torrefied wood reveals distinctive temperature peaks at 323 °C and 466 °C. The first peak (at 323 °C) is considered a precursor to the main peak, while the second peak (at 466 °C) indicates a diverse range of compounds, consistent with the high content of volatile
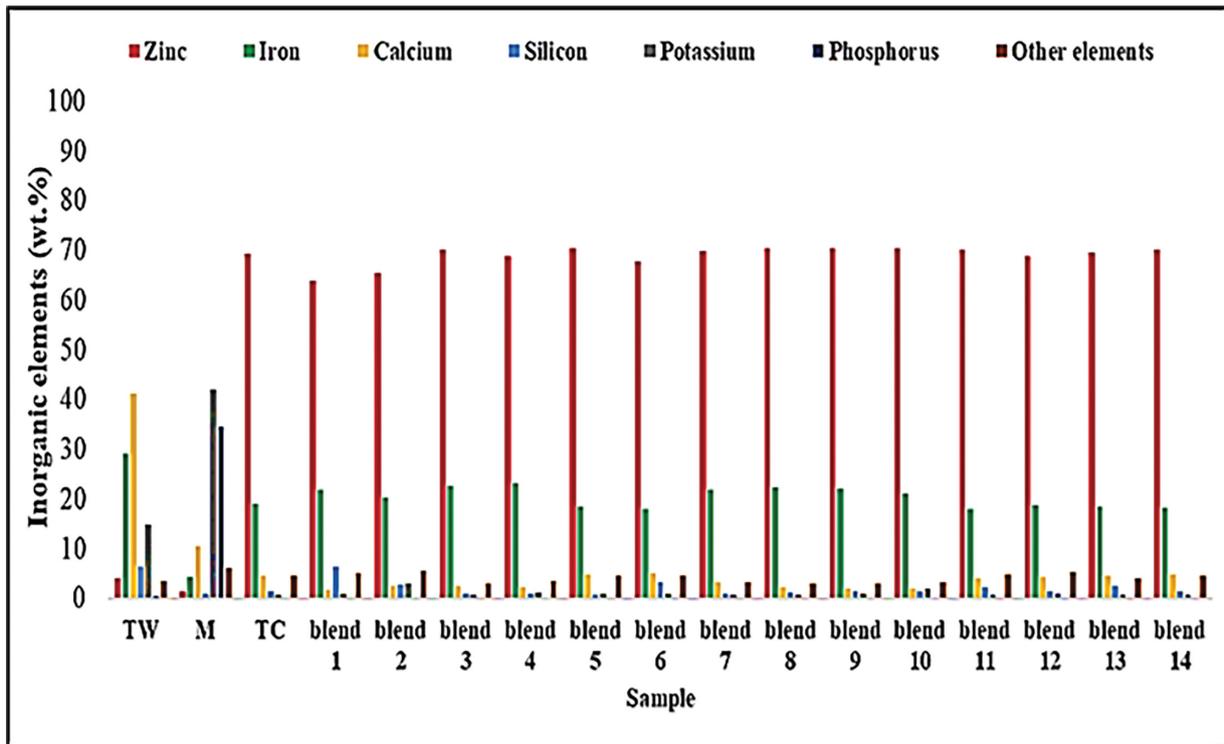
TW, torrefied wood; M, microalgae; TC, tyre char

Figure 1: The main inorganic elements (%) present in the parent fuel and various blends of char.

TC, tyre char; TW, torrefied wood; M, microalgae

Figure 2: Mass loss and derivative thermogravimetric (DTG) curves of parent fuels.

matter in torrefied wood.[26] The first thermal event involves simultaneous ignition and decomposition of cellulose, along with ignition of lignin as elucidated by López-González et al.[27] Cellulose decomposition is completed around 400 °C, leading to the main decomposition of lignin and fixed carbon in the second event. The burnout temperature at 518 °C is a common feature of torrefied wood combustion, attributed to the high reactivity of biomass. This increased the reactivity with rising

combustion temperature related to elevated volatile matter content while influencing ignition behaviour and enhancing particle surface reactivity.[28]

The thermal decomposition of the tyre char is mainly characterised by two distinct peaks within the combustion region of the char (500–600 °C), which are associated with the combustion of fixed carbon. The high ignition temperature of 546 °C was anticipated because components of the tyre with lower thermal stability were released as volatiles during the

Table 2: Combustion characteristics of raw and blended char samples

Blend	First thermal event				Second thermal event			Third thermal event			T_b (°C)
	T_i (°C)	T_o (°C)	T_p (°C)	DTG$_{max}$ (%/°C)	T_o (°C)	T_p (°C)	DTG$_{max}$ (%/°C)	T_o (°C)	T_p (°C)	DTG$_{max}$ (%/°C)	
TC	425	–	–	–	531	538	2.24	546	554	1.02	635
TW	248	299	323	0.22	388	466	0.85	–	–	–	518
M	152	239	290	0.40	418	520	0.24	560	620	0.15	640
1	208	249	319	0.25	410	508	0.33	534	567	0.49	634
2	211	242	321	0.29	412	488	0.23	532	574	0.88	638
3	250	271	291	0.03	411	501	0.33	539	564	0.83	638
4	206	247	323	0.11	422	502	0.31	530	565	0.75	642
5	291	318	342	0.10	422	488	0.42	526	550	0.85	624
6	292	318	345	0.14	418	493	0.43	538	562	0.84	622
7	266	–	–	–	427	500	0.33	536	570	0.78	640
8	228	280	333	0.15	425	490	0.29	533	575	0.82	645
9	221	243	327	0.16	–	–	–	528	560	0.99	629
10	221	244	323	0.13	–	–	–	528	565	0.78	638
11	323	–	–	–	–	–	–	521	552	1.32	625
12	276	–	–	–	412	484	0.43	515	558	0.78	617
13	296	–	–	–	538	544	1.82	531	564	0.79	619
14	295	–	–	–	530	540	1.80	525	549	0.70	611

T_i, initial decomposition temperature; T_o, peak onset temperature; T_p, maximum peak temperature at each thermal event; DTG$_{max}$, maximum weight loss rate for each peak; T_b, burn out temperature of sample; TC, tyre char; TW, torrified wood; M, microalgae

pyrolysis process. The first peak, marked by a higher mass loss, can be attributed to the separate combustion of the tyre char and chemisorbed complexes such as carboxylic, quinonic and/or phenolic groups found on the surface of carbon blacks. The second peak represents the combustion of graphite-like material.[29]

Thermogravimetric mass loss and derivative thermogravimetric curves of blended char–biomass samples are shown in Figure 3. In Figure 3a, the differential thermogravimetric profiles of binary mixtures containing 10 wt% of torrefied wood exhibit a distinct pattern that resembles the combustion behaviour of tyre char. In contrast, for binary blends comprising 30 wt%. For torrefied biomass, the differential thermogravimetric profiles exhibit two discernible peaks and elevated rates of mass loss. As the proportion of torrefied wood increases, the ignition temperature decreases, mainly because of the early release of volatile components at lower temperatures. This lowered ignition temperature facilitates the initiation of combustion processes.[16]

The initial peak corresponds to the decomposition of torrefied wood, while the second, more pronounced peak, occurring above 500 °C, represents the combustion of tyre char. In particular, the mass loss rate during the second peak in binary blends with 30 wt%. The torrefied wood loading was comparatively lower than that of tyre char alone. This finding is attributed to the reduced content of fixed carbon in these blends within the temperature range of 550–650 °C. In general, an increase in the torrefied biomass ratio leads to enhanced reactivity of the blends. In Figure 3b, the impact of the addition of microalgae was inconspicuous at low microalgae ratios. Ternary blends containing 15–30 wt% torrefied wood and 4–11 wt% microalgae closely resemble the combustion behaviour of binary blends with 30 wt% torrefied wood (Figure 3a).

In particular, the blend labelled TC70-TW30-M0 showed a delayed initial decomposition temperature, an indistinct bridge preceding the combustion of char, the maximum mass loss rate during the combustion phase of the char and a lower ignition temperature of the char compared to other blends. An increase in the microalgae ratio results in a further rightward shift of the char combustion peaks. This phenomenon can be attributed to the elevated ash content of the microalgae and the gas-phase products of volatile combustion, which retard the ignition of tyre char in the blends.[30] Similarly, the burn-out temperature increases with an elevation in the microalgae ratio, indicating an extended combustion duration.

In Figure 3c, tyre char and blends consisting of 10–30 wt% torrefied wood, with a maximum microalgae content of 15 wt%, are depicted. The decomposition temperature of the fuel blends with 15 wt% microalgae and 20–30 wt% of torrefied wood loading is significantly lower compared to other char blends. The primary combustion event in these fuel mixtures shifts to the right, resulting in an approximately 10 °C increase in the burn-out temperature. The combustion peaks are broader and shorter for these blends, indicating increased material diversity and enhanced reactivity compared to the combustion of tyre char alone. A similar observation was reported by Xinjie et al.[15] who found that increasing the biomass ratio increased the reactivity of the tri-fuel blend. Similarly, Jayaraman et al.[17] noted that high biomass proportions (25–75 wt%) enhanced the reactivity of blended samples during combustion. The results of this study regarding biomass addition are consistent with the findings of Slyusarsky et al.[18], who demonstrated similar effects during the thermal decomposition of tyre char with peat and tyre char with pine sawdust mixtures.

Gas evolution profiles by mass spectroscopy

The gas evolution profiles of the parent samples are shown in Figure 4a–c. The gases analysed were carbon dioxide (CO_2) (m/e 44), nitrogen dioxide (NO_2) (m/e 46) and sulfur dioxide (SO_2) (m/e 64). Raw fuels are low emitters of NO_2 and SO_2, as highlighted by low counts in the evolution of the respective gases. Despite the low count of NO_2, the mass spectra show a strong NO_2 peak for the torrefied biomass, although the torrefied biomass was found to have lower amounts of nitrogen, as highlighted in
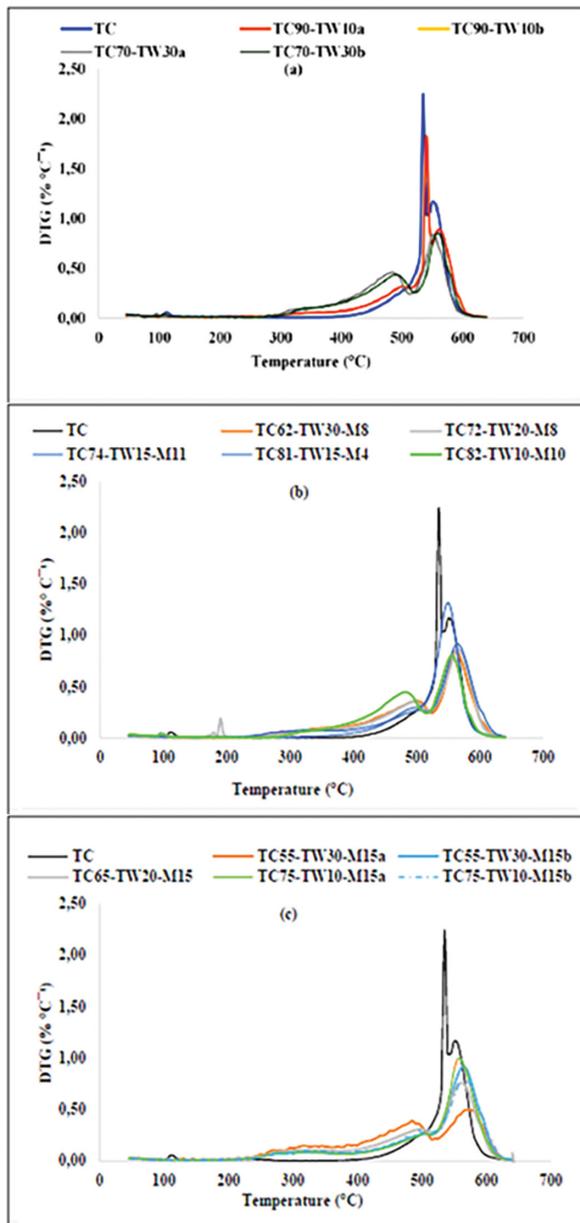
Figure 3: Derivative thermogravimetric (DTG) curves for the blends with (a) 0% microalgae, (b) 4–11% microalgae and (c) 15% microalgae.

Figure 4: Mass spectra of gas evolution during combustion of parent fuels: (a) CO_2 emission, (b) NO_2 emission and (c) SO_2 emission.

Table 1. Changes in the nitrogen contained in torrefied wood may require further investigation to understand the consistent release of NO_2 during its combustion due to the intensity of the peak of NO_2. The emission of CO_2 shows distinct peaks in tyre char and torrefied wood. A further look at the emission of CO_2 during the combustion of binary and ternary char–biomass blends is shown in Figure 5. The mass spectroscopy curves presented in Figure 5a–c exhibit a consistent profile in terms of shape and temperature range, as depicted by the corresponding derivative thermogravimetric curves discussed earlier. This uniformity in the profiles suggests that the evolution of CO_2 occurred at the same peak temperatures and during each thermal event for all the materials examined. These findings align with those reported by Magida et al.[11] Notably, the co-combustion of the binary blends of torrefied biomass and tyre char resulted in significant CO_2 emissions, as expected. The raw materials (tyre char and torrefied wood) contain substantial amounts of elemental carbon, with torrefied biomass containing 76 wt% and tyre char containing 90 wt%. It should be noted that the peak CO_2 observed during torrefied wood combustion exceeds that of tyre char combustion. This suggests that the release of CO_2 in torrefied wood combustion
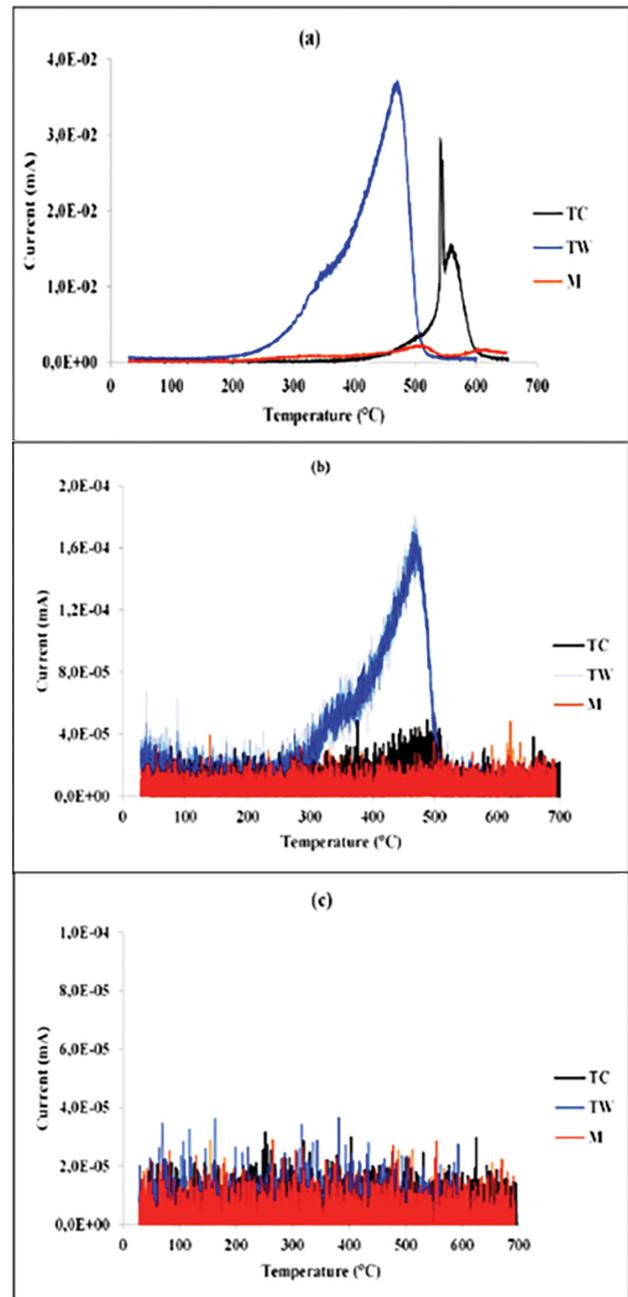
occurs in both the volatile decomposition and char combustion phases. Consequently, it implies that the combustion of tyre chars emits a lesser amount of CO_2 compared to torrefied wood combustion. The combustion of ternary char–biomass blends with 15 wt% and 20 wt% loading of torrefied wood results in lower emission peaks in the 500–600 °C range compared to raw tyre char. This implies a lower release of CO_2 emissions during the combustion of these ternary char–biomass blends with high torrefied wood loading compared to the combustion of tyre char alone. This reduction in the strength of the CO_2 peak as biomass loading increases is consistent with the findings reported in previous studies.[11,31] However, binary blends containing the least amount of torrefied wood exhibit higher CO_2 emission peaks above 500 °C compared to tyre char. The high evolution of CO_2 in this combustion stage is influenced by differences in the fixed carbon and ash compositions within the blended samples.[17] Slyusarsky et al.[18] observed that increasing the proportion of pine sawdust in the tyre char/pine sawdust blend from 5 wt% to 15 wt% led to an increase in CO_2 formation, with CO_2 emission peaks exceeding
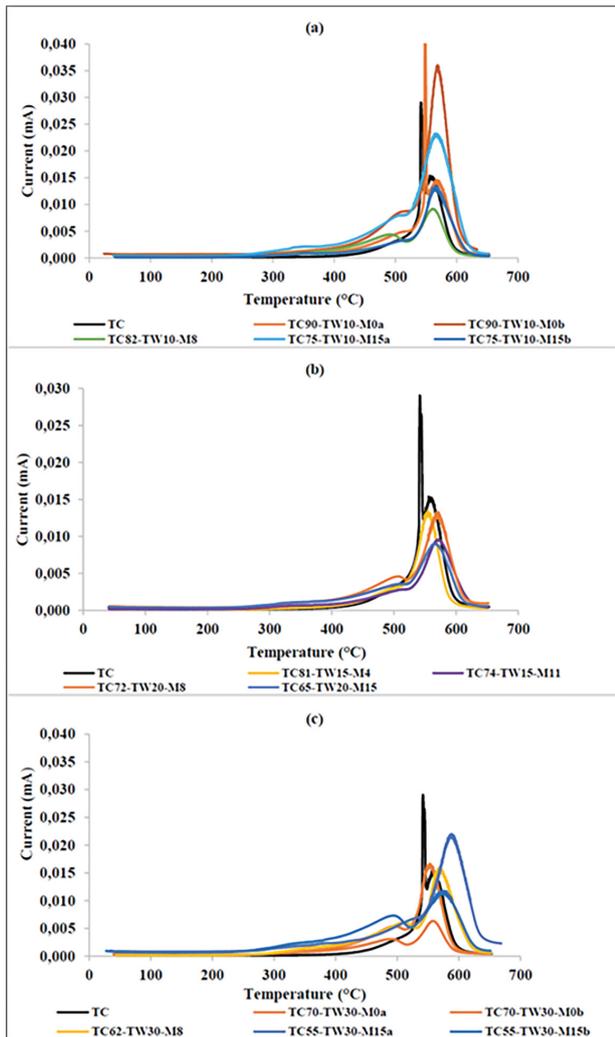
Figure 5: Mass spectra of CO_2 evolution during combustion of tyre char–biomass blends: (a) 10% torrefied wood, (b) 15–20% torrefied wood and (c) 30% torrefied wood.

those from the combustion of tyre char alone. In contrast, for tyre char/peat mixtures, the intensity of CO_2 formation decreased as the biomass (peat) ratio increased.

Conclusions

Based on the physicochemical and combustion characteristics of the binary and ternary blends, it is apparent that biomass material influences the physicochemical properties of tyre char, consequently impacting the combustion characteristics of these chars. In particular, an increase in the microalgae content within ternary blends resulted in a shift in combustion peaks and burnout temperatures, thereby prolonging the combustion phase as compared to the combustion of tyre char alone. Furthermore, it has been observed that biomass additions in various ratios have a significant effect on the reduction of CO_2 emission patterns.

This study has demonstrated that blending tyre char with biomass, especially at increased biomass ratios, enhances the combustion characteristics of tyre char. Consequently, a mixture of tyre char and biomass has the potential to serve as an environmentally friendly combustion fuel. Therefore, tyre char–biomass blends can be considered for cleaner combustion processes. For future studies, we recommend a techno-economic analysis of tyre char blends to evaluate the economic feasibility of such fuel blends. Additionally, future investigations should focus on the large-scale combustion of tyre char–biomass blends as well as explore pelletisation or briquetting methods for agglomerating such char blends.

Data availability

The data supporting the results of this study are available upon request to the corresponding author.

Declarations

We have no competing interests to declare. We have no AI or LLM use to declare.

Authors' contributions

C.T.D.: Writing – the initial draft, data collection, sample analysis, data analysis, validation. H.B.: Conceptualisation, methodology, writing – the initial draft, writing – revisions, student supervision. Both authors read and approved the final manuscript.

References

1. Tang H, Hu H, Li A, Yi B, Li X, Yao D, et al. Removal of impurities from waste tire pyrolysis char using the molten salt thermal treatment. Fuel. 2021;301, Art. #121019. https://doi.org/10.1016/j.fuel.2021.121019

2. Ren Q, He L, Hu S, Su S, Wang Y, Jiang L, et al. The structural characteristics of waste tire chars at different pyrolysis temperatures. IOP Conf Ser Earth Environ Sci. 2021;657(1), Art. #012005. https://doi.org/10.1088/1755-1315/657/1/012005

3. Yaru SS, Satope PO, Akinola AO. Characterization of char from waste tyre pyrolysis. Saudi J Eng Technol. 2021;6(7):169–177. https://doi.org/10.36348/sjet.2021.v06i07.004

4. Jahirul MI, Hossain FM, Rasul MG, Chowdhury AA. A review on the thermochemical recycling of waste tyres to oil for automobile engine application. Energies. 2021;14(13), Art. #3837. https://doi.org/10.3390/en14133837

5. Sarawan S, Wongwuttanasatian T. A feasibility study of using carbon black as a substitute to coal in cement industry. Energy Sustain Dev. 2013;17(3):257–260. https://doi.org/10.1016/j.esd.2012.11.006

6. Qiao Y, Chen Z, Wu X, Zheng Y, Guan S, Li J, et al. Analysis of comprehensive utilization of waste tire pyrolysis char by combustion method. Fuel. 2022;312, Art. #122996. https://doi.org/10.1016/j.fuel.2021.122996

7. 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. 2014;119:263–271. https://doi.org/10.1016/j.fuproc.2013.11.015

8. Hu H, Fang Y, Liu H, Yu R, Luo G, Liu W, et al. The fate of sulfur during rapid pyrolysis of scrap tires. Chemosphere. 2014;97:102–107. https://doi.org/10.1016/j.chemosphere.2013.10.037

9. Ye B, Zhang R, Cao J, Lei K, Liu D. The study of co-combustion characteristics of coal and microalgae by single particle combustion and TGA methods. J Energy Inst. 2020;93(2):508–517. https://doi.org/10.1016/j.joei.2019.07.001

10. Gaqa SG, Watts P. The agglomeration of coal fines using wet microalgae biomass. J Energy South Afr. 2018;29(2):43–50. https://doi.org/10.17159/2413-3051/2018/v29i2a3469

11. Magida NE, Bolo LL, Hlangothi SP, Dugmore G, Ogunlaja AS. Co-combustion characteristics of coal-*Scenedesmus* microalgae blends and their resulting ash. Combust Sci Technol. 2021;193(3):419–436. https://doi.org/10.1080/00102202.2019.1658577

12. Ejesieme VO, Riaza J, Vorster N, Dugmore G, Zeelie B. Reclamation of ultra-fine coal with *Scenedesmus* microalgae and comprehensive combustion property of the Coalgae® composite. J Energy S Afr. 2020;31(1):14–27. https://dx.doi.org/10.17159/2413-3051/2020/v31i1a6430

13. Tumuluru JS, Ghiasi B, Soelberg NR, Sokhansanj S. Biomass torrefaction process, product properties, reactor types, and moving bed reactor design concepts. Front Energy Res. 2021; 9, Art. #728140. https://doi.org/10.3389/fenrg.2021.728140

14. Okoro N-JM, Ozonoh M, Harding KG, Oboirien BO, Daramola MO. Potentials of torrefied pine sawdust as a renewable source of fuel for pyro-gasification: Nigerian and South African perspective. ACS Omega. 2021;6(5):3508–3516. https://doi.org/10.1021/acsomega.0c04580

15. Xinjie L, Singh S, Yang H, Wu C, Zhang S. A thermogravimetric assessment of the tri-combustion process for coal, biomass and polyethylene. Fuel. 2021;287, Art. #119355. https://doi.org/10.1016/j.fuel.2020.119355

16. Mundike J, Collard F-X, Görgens JF. Co-combustion characteristics of coal with invasive alien plant chars prepared by torrefaction or slow pyrolysis. Fuel. 2018;225:62–70. https://doi.org/10.1016/j.fuel.2018.03.024

17. Jayaraman K, Kok MV, Gokalp I. Thermogravimetric and mass spectrometric (TG-MS) analysis and kinetics of coal-biomass blends. Renew Energy. 2017;101:293–300. https://doi.org/10.1016/j.renene.2016.08.072

18. Slyusarsky K, Tolokolnikov A, Gubin A, Kaltaev A, Gorshkov A, Asilbekov A, et al. Ignition and emission characteristics of waste tires pyrolysis char co-combustion with peat and sawdust. Energies. 2023;16(10), Art. #4038. https://doi.org/10.3390/en16104038

19. Undri A, Sacchi B, Cantisani E, Toccafondi N, Rosi L, Frediani M, et al. Carbon from microwave-assisted pyrolysis of waste tires. J Anal Appl Pyrolysis. 2013;104:396–404. https://doi.org/10.1016/j.jaap.2013.06.006

20. Farrow TS, Sun C, Snape CE. Impact of biomass char on coal char burn-out under air and oxy-fuel conditions. Fuel. 2013;114:128–134. https://doi.org/10.1016/j.fuel.2012.07.073

21. Kazagic A, Smajevic I. Experimental investigation of ash behavior and emissions during combustion of Bosnian coal and biomass. Energy. 2007;32(10):2006–2016. https://doi.org/10.1016/j.energy.2007.03.007

22. Sahu SG, Chakraborty N, Sarkar P. Coal-biomass co-combustion: An overview. Renew Sustain Energy Rev. 2014;39:575–586. https://doi.org/10.1016/j.rser.2014.07.106

23. Kebelmann K, Hornung A, Karsten U, Griffiths G. Intermediate pyrolysis and product identification by TGA and Py-GC/MS of green microalgae and their extracted protein and lipid components. Biomass Bioenergy. 2013;49:38–48. https://doi.org/10.1016/j.biombioe.2012.12.006

24. Tahmasebi A, Kassim MA, Yu J, Bhattacharya S. Thermogravimetric study of the combustion of *Tetraselmis suecica* microalgae and its blend with a Victorian brown coal in O_2/N_2 and O_2/CO_2 atmospheres. Bioresour Technol. 2013;150:15–27. https://doi.org/10.1016/j.biortech.2013.09.113

25. Ross AB, Jones JM, Kubacki ML, Bridgeman T. Classification of macroalgae as fuel and its thermochemical behaviour. Bioresour Technol. 2008;99(14):6494–6504. https://doi.org/10.1016/j.biortech.2007.11.036

26. Toptas A, Yildirim Y, Duman G, Yanik J. Combustion behavior of different kinds of torrefied biomass and their blends with lignite. Bioresour Technol. 2015;177:328–336. https://doi.org/10.1016/j.biortech.2014.11.072

27. López-González D, Fernandez-Lopez M, Valverde JL, Sanchez-Silva L. Thermogravimetric-mass spectrometric analysis on combustion of lignocellulosic biomass. Bioresour Technol. 2013;143:562–574. https://doi.org/10.1016/j.biortech.2013.06.052

28. Moon C, Sung Y, Ahn S, Kim T, Choi G, Kim D. Effect of blending ratio on combustion performance in blends of biomass and coals of different ranks. Exp Therm Fluid Sci. 2013;47:232–240. https://doi.org/10.1016/j.expthermflusci.2013.01.019

29. Sahouli B, Blather S, Brouers F, Darmstadtt H, Royt C, Kaliaguinet S. Surface morphology and chemistry of commercial carbon black and carbon black from vacuum pyrolysis of used tyres. Fuel. 1996;75(10):1244–1250. https://doi.org/10.1016/0016-2361(96)00034-8

30. Sami M, Annamalai K, Wooldridge M. Co-firing of coal and biomass fuel blends. Prog Energy Combust Sci. 2001;27(2):171–214. https://doi.org/10.1016/S0360-1285(00)00020-4

31. Zhang Y, Guo Y, Cheng F, Yan K, Cao Y. Investigation of combustion characteristics and kinetics of coal gangue with different feedstock properties by thermogravimetric analysis. Thermochim Acta. 2015;614:137–148. https://doi.org/10.1016/j.tca.2015.06.018