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Thermogravimetric and physicochemical characterization of waste tire–coconut shell blends as potential renewable energy feedstock

Samsudin Anis,^{*a} Sukarni Sukarni,^b Alavudeen Azeez,^c Ahmad Indra Siswantara,^d Sonika Maulana,^a Deni Fajar Fitriyana,^a Adhi Kusumastuti,^e Januar Parlaungan Siregar,^{f,g} Sivasubramanian Palanisamy,^h Aravindhan Alagarsamy,ⁱ Mohamed Abbas,^{j,k} Shaeen Kalathil^l and Mezigebu Belay^m

The global energy crisis caused by population increase and industrialization has prompted the exploration of more sustainable renewable energy sources. The utilization of organic and inorganic waste as an alternative energy source is emerging as a potential solution that can reduce dependence on fossil fuels. The present study investigates the thermogravimetric and physicochemical characteristics of blends derived from waste tires and coconut shells, emphasizing their viability as sustainable energy sources. Specimens consisting of different ratios of tire waste and coconut shells, designated as CS100WT0, CS75WT25, CS50WT50, CS25WT75, and CS0WT100, underwent analysis through thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and calorific value testing. The results demonstrate that augmenting the percentage of waste tires in the mixture significantly affects the thermal degradation, functional groups, crystalline phases, and calorific value of the material. The maximum temperature (T_{\max}) reached by CS100WT0 was 325 °C, suggesting superior thermal stability compared to the other specimens. However, the T_{\max} of CS75WT25, CS50WT50, and CS25WT75 increased as the content of waste tires increased. The incorporation of waste tires leads to a diminished intensity of the O–H functional group, indicating a reduction in moisture content and enhanced energy production efficiency. The calorific value of the specimens elevated with the elevated content of waste tires. The CS25WT75 specimen exhibited the highest calorific value of 27.75 MJ kg⁻¹, indicating that it has a higher energy potential compared to blends with a higher proportion of coconut shells. This research improves waste-to-energy technologies that mitigate pollution, promote resource recovery, and offer sustainable alternatives to conventional energy sources. This research is consistent with several Sustainable Development Goals (SDGs), specifically Goal 7, which focuses on Affordable and Clean Energy, and Goal 12, which emphasizes Responsible Consumption and Production.

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^aDepartment of Mechanical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang, 50229, Indonesia. E-mail: samsudin_anis@mail.unnes.ac.id

^bCenter for Renewable Fuels Research (CRFR), Department of Mechanical and Industrial Engineering, Universitas Negeri Malang, Malang, 65145, Indonesia

^cDepartment of Mechanical Engineering, Kalasalingam Academy of Research and Education, Krishnankoil-626126, Tamil Nadu, India

^dMechanical Engineering Department, Faculty of Engineering, Universitas Indonesia, Depok, 16424, Indonesia

^eFaculty of Engineering, Universitas Negeri Semarang, Semarang, 50229, Indonesia

^fCentre for Automotive Engineering, Universiti Malaysia Pahang Al-Sultan Abdullah (UMPSA), 26600 Pekan, Pahang, Malaysia

^gFaculty of Mechanical & Automotive Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Pekan 26600, Malaysia

^hDepartment of Mechanical Engineering, School of Engineering, Mohan Babu University, Tirupati - 517102, Andhra Pradesh, India. E-mail: sivaresearch948@gmail.com

ⁱCenter for Flexible Electronics, Department of Electronics and Communication Engineering, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Andhra Pradesh, 522501, India

^jDepartment of Electrical Engineering, College of Engineering, King Khalid University, Abha 61421, Saudi Arabia

^kDepartment of Condensed Matter Physics, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences (SIMATS), Thandalam, Chennai, India

^lDepartment of Electrical Engineering, College of Engineering, Princess Nourah bint Abdulrahman University, P. O. Box 84428, Riyadh 11671, Saudi Arabia

^mDepartment of Metallurgical and Materials Engineering, College of Engineering, Ethiopian Defence University, Bishoftu, 1041, Ethiopia. E-mail: mezgebubelay@etdu.edu.et



Sustainability Spotlight

This research advances the circular economy by valorizing organic (coconut shells) and inorganic (waste tires) residues into high-energy potential fuels, reducing reliance on fossil-based energy systems. Through thermochemical characterization and optimization of waste-derived blends, it contributes to cleaner energy production with reduced environmental burden. The findings directly support the United Nations Sustainable Development Goals (SDG 7: Affordable and Clean Energy and SDG 12: Responsible Consumption and Production) by promoting resource recovery, minimizing waste disposal, and enhancing renewable energy pathways.

1 Introduction

Significant challenges regarding energy availability are currently confronting the global community. This can be attributed to the exponential increase in population and explosive industrialization.^{1,2} Global reliance on fossil fuels, such as oil, natural gas, and coal, contributes to the depletion of natural resource reserves and severe climate change caused by greenhouse gas emissions.^{3–5} Nonetheless, efforts to shift from fossil fuels to renewable energy sources consistently must overcome numerous obstacles. Renewable energy technologies are continuously advancing, including solar, wind, and hydro-power plants.^{6–10}

Nevertheless, the extensive implementation of these technologies is hindered by obstacles related to location, energy density, transport restrictions, intermittency, land availability, finances, and environmental footprint.¹¹ Conversely, the quantity of waste (including organic and inorganic materials) produced by human activities consistently increases annually. Inadequate management of these wastes presents a substantial environmental risk in the future.¹² Consequently, it is necessary to conduct a study to examine the use of organic and inorganic waste produced by human activities as a substitute form of renewable energy that is both ecologically sustainable and capable of decreasing reliance on finite natural resources.¹³

Utilizing waste for electricity production has various benefits, such as mitigating environmental pollution, scaling back greenhouse gas emissions, enhancing waste's value and economic viability, mitigating health hazards and generating employment opportunities for the residents of the region.¹⁴ Nevertheless, the primary obstacle linked to using waste for energy is determining the ideal combination of garbage that yields optimum energy efficiency and minimal environmental impact. It is imperative to acknowledge that not all categories of waste possess the requisite attributes appropriate for fuel generation. Consequently, a thorough investigation is necessary to determine the precise waste category and the most efficient approach for its conversion.

Coconut shells are an abundant biomass waste resource extensively distributed in tropical nations, including Indonesia, the Philippines, and India.

Every year, the coconut processing industry produces millions of tons of broken coconut shells as waste. In 2024, Indonesia's coconut shell production reached 338 640 000 metric tons.¹⁵ Inappropriate use of coconut shells could lead to their indiscriminate incineration or degradation, thereby exacerbating environmental contamination. From an energy standpoint, coconut shells have significant potential due to their high calorific content of 4523 kcal kg⁻¹ or 17.40 MJ kg⁻¹.^{16,17} The carbonaceous nature of coconut shells, as well as

their abundant lignin and cellulose content, makes them an excellent raw material for energy conversion by pyrolysis or direct burning. Coconut shells can undergo pyrolysis to produce charcoal, tar, and gas, all of which can serve as fossil fuels.^{18–21} Furthermore, this method may also generate activated carbon, which possesses significant economic worth. Further advantages of coconut shells are their high disintegration rate and non-toxic nature, making energy conversion processes related to coconut shells cleaner and more ecologically sustainable than those of fossil fuels.

The extensive use of rubber tires and other rubber products worldwide has resulted in substantial quantities of non-biodegradable rubber waste. Inadequate management of this substance will have economic and environmental consequences. Approximately 1.5 billion tires are sold globally annually, with more than half discarded without treatment. Projections indicate that by 2030, the yearly production of old tires will reach 1200 million.²² Often, people dispose of waste tires indiscriminately or illegally incinerate them, resulting in wastewater, air, and soil pollution. Tires undergo biodegradation for several centuries, posing a persistent environmental risk when deposited in landfills. As a result, the world is confronted with the formidable global challenge of recycling the substantial volume of tire waste generated. Generally, tires possess substantial carbon content and calorific indices. Tires have a calorific value of 35–39 MJ kg⁻¹, equal to lump coal's calorific value.^{22,23} This attribute makes waste tires extremely promising for use as a sustainable energy resource.^{22–25} Nevertheless, using used tires as a source of energy still raises concerns about the release of contaminants, such as sulfur and heavy metals, during combustion or pyrolysis.²⁶ Hence, it is crucial to ascertain efficient strategies to mitigate these negative effects, including integrating waste tires with biomass materials like coconut shells.

Experimental studies on using waste as a renewable energy source have demonstrated considerable promise. Numerous studies have focused exclusively on a single category of waste, such as waste tires or biomass, disregarding the potential synergies resulting from the amalgamation of both types of waste. Research on combining waste tires with biomass, like coconut shells, remains limited, especially when it comes to understanding the thermal and chemical properties of these blends during the pyrolysis or combustion process. Therefore, this study aims to examine the viability of using a blend of waste tires and coconut shells as a renewable energy production material. This study is designed to determine and delineate the thermogravimetric and physicochemical characteristics of the mixture of these two waste products. Furthermore, this research is expected to significantly advance the exploration of green renewable energy sources and improve green waste management systems.



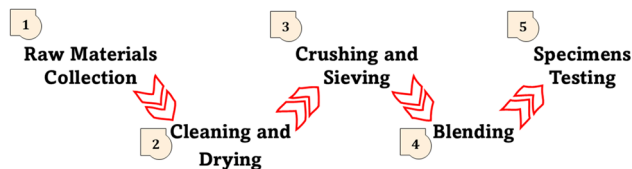


Fig. 1 The experimental setup.

2 Materials and methods

The experimental setup in this study is presented in Fig. 1. This study utilized coconut shells and waste tires collected from nearby areas of the Universitas Negeri Semarang campus in Indonesia. To eliminate grime and dust, both materials were meticulously cleaned through washing. Subsequently, the coconut shells and waste tires were exposed to the sun for 2 days until they completely dried. The dried materials were subsequently crushed separately using a crusher machine. The fine powder was produced by sieving the crushed material through a sieve with a mesh size of 80, as shown in Fig. 2. The coconut shell and waste tire powders were subsequently blended with a variety of compositions. Table 1 displays the code and composition of the specimens employed in this investigation.

This study utilized a mechanical mixer operating at a low speed (500–1000 rpm) to prevent aggregation of the waste tire and coconut shell powders. The mixing procedure was conducted for 30 minutes to guarantee a homogeneous mixture. Prior to testing, a blend of used tire and coconut shell powder was dried in an oven at 100 °C for 4 hours. This process removes moisture from the materials, ensuring that they are in optimal condition for subsequent testing.²⁷

The blended material was subjected to calorific value testing, thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). These tests aimed to assess the impact of the composition of a blend of coconut shell

Table 1 The code and composition of the specimens

Specimen codes	Compositions (wt%)	
	Coconut shells	Waste tire
CS100WT0	100	0
CS75WT25	75	25
CS50WT50	50	50
CS25WT75	25	75
CS0WT100	0	100

and waste tire on the calorific value, thermal characteristics, T_{\max} , crystal phase, and functional groups of each sample.

A bomb calorimeter was used to test the specimens' calorific value following ASTM D-240.¹⁵ The process entails igniting a precisely measured sample within a high-pressure steel blast containing pure oxygen. The bomb is encased in a water jacket, enabling the heat generated during combustion to be entirely absorbed by the water, resulting in a quantifiable temperature rise. The increase in temperature, along with the calorimeter's calibrated heat capacity, enables accurate assessment of the sample's calorific value. Calibrating the bomb calorimeter is crucial for ascertaining the calorimeter constant (ϵ), translating the temperature variation into energy quantified in J/K . The calibration is performed by burning benzoic acid (BA), an appropriate substance with a known calorific value. The energy emitted by BA is divided by the adjusted temperature rise, accounting for energy adjustments from fuse wire combustion, ignition wire oxidation, and nitric acid production.²⁸

The Simultaneous Thermogravimetric Analyzer (STA7000 series), manufactured by Hitachi Ltd (Tokyo, Japan), was employed to conduct TGA and DTG tests. Samples weighing 6.632 mg were tested using an initial temperature range of 30 °C to 700 °C, a heating rate of 10 °C per minute, and a nitrogen gas flow rate of 100 mL per minute. Data from the TGA and DTG tests include measurements of temperature change and mass loss of the specimen, which offer insights into the material's thermal stability and degradation rate.²⁹ The selection of

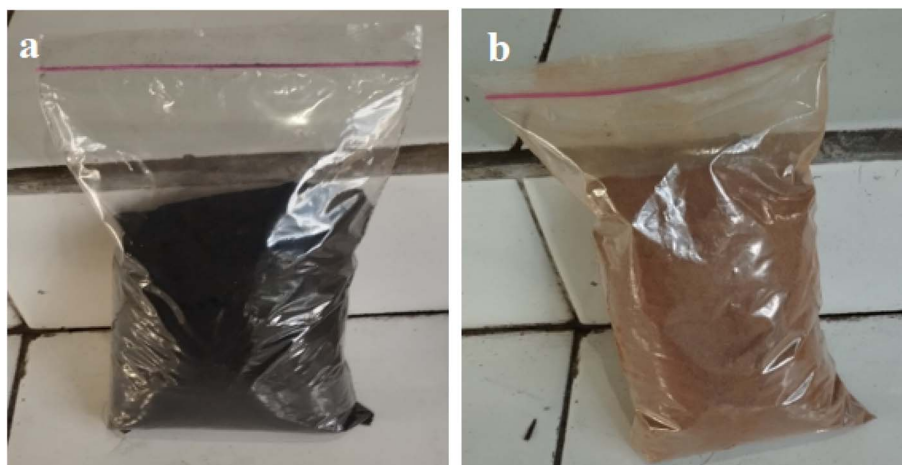


Fig. 2 Powders obtained from (a) waste tires and (b) coconut shells.



a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ is justified by the research conducted by Pan *et al.*,²⁷ which involved Thermogravimetric Analysis (TGA) of coal and waste tire blends at heating rates of 10, 20, and $40\text{ }^{\circ}\text{C min}^{-1}$. The study concluded that a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ is the most representative for laboratory-based combustion characteristic investigations. This low rate allows sufficient time for consistent heat penetration into the sample, leading to more accurate thermal data (*e.g.*, ignition and burnout temperatures), which more accurately represent the natural characteristics of the fuel, especially in blends with components that are challenging to break down, such as waste tires (WT).

X-ray diffraction (XRD) analysis was conducted on the specimens using XRD-7000 Series X-ray diffractometers manufactured by Shimadzu Corporation in Kyoto, Japan. The machine's operational parameters included a voltage of 40 kV and a current of 30 mA. The machine utilized $\text{CuK}\alpha$ radiation with a wavelength of 1.54056. The studies were conducted within an angle range of 20° to 80° , with a precision of 0.02° increments and a scan rate of 2° per minute. An analysis was conducted on the XRD patterns of the materials acquired from each specimen to identify and measure the crystal phase using the ICDD (the International Centre for Diffraction Data) database.³⁰ This study employed Fourier Transform Infrared (FTIR) research to ascertain the existence and characteristics of chemical functional groups inside the presented specimen. The FTIR analysis was conducted using a PerkinElmer (CT, USA) FTIR spectrometer system. FTIR spectra were acquired by measuring wavelengths within the infrared range from 400 to 4000 cm^{-1} . A spectral resolution of 2 cm^{-1} was achieved by conducting measurements at 200 scans per second.^{30,31}

3 Results and discussion

Fig. 3 displays the results of TGA testing conducted on each specimen. A classification and evaluation of the proximate analysis of each material was undertaken in this study. Furthermore, this methodology was also employed to ascertain the devolatilization properties that manifested in each sample. The mass reduction of each specimen was quantified and graphed as a function of temperature. The specimen consisting of 100% waste tire (CS0WT100) begins to degrade at approximately $250\text{ }^{\circ}\text{C}$. At this temperature, the specimen undergoes a mass reduction of 1.53%, attributable to the evaporation of the humidity present in the waste tire. Consequently, throughout a temperature range of $250\text{ }^{\circ}\text{C}$ to $310\text{ }^{\circ}\text{C}$,³² decomposition of the oil, plasticizers, and additives in the tire occurs, leading to a mass loss of 27.88%. Within the temperature interval of $310\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$,³² natural rubber and styrene-butadiene degradation transpires, resulting in a mass loss of 36.65%. Upon completion of the degradation process at $700\text{ }^{\circ}\text{C}$, the residual mass of the CS0WT100 specimen constitutes 33.94% of its initial weight.

This study's results demonstrate that the total mass loss in the CS0WT100 specimen is around 66.04%. This study produced less residue than that of Moulin *et al.*,³³ who recorded a waste tire residue of 38% during their TGA test. The research

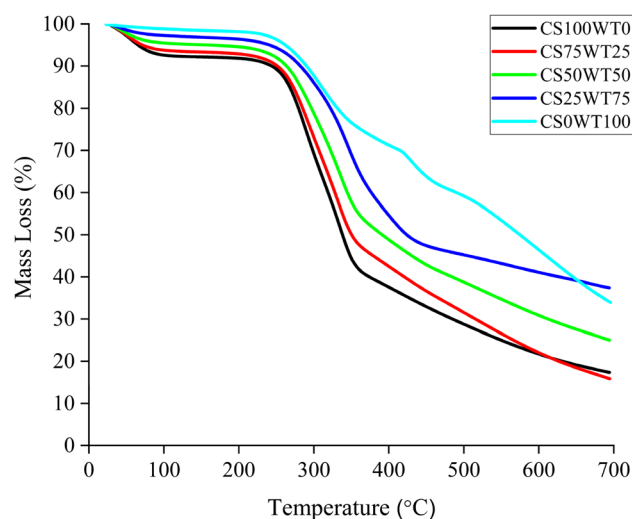


Fig. 3 TGA test results for each specimen.

conducted by Moulin *et al.*³³ demonstrated that the breakdown of waste tires commences at $150\text{ }^{\circ}\text{C}$, with minimal weight loss until reaching $300\text{ }^{\circ}\text{C}$, a phenomenon ascribed to the volatility of additives like plastics and processing oils. Subsequently, in the temperature range of $300\text{ }^{\circ}\text{C}$ to $575\text{ }^{\circ}\text{C}$, the predominant weight loss transpires, linked to the degradation of rubber, particularly between $350\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$, encompassing the disintegration of essential constituents such as SBR (styrene-butadiene rubber), NR (natural rubber), and BR (butadiene rubber). Their research demonstrated that the deterioration of the waste tire specimen is complete at $550\text{ }^{\circ}\text{C}$, with no additional weight loss detected at elevated temperatures.

Kumar *et al.*³² indicated that the thermogravimetric analysis of waste tires reveals that degradation initiates at $235\text{ }^{\circ}\text{C}$. The tire material experiences degradation in two separate phases: from $250\text{ }^{\circ}\text{C}$ to $310\text{ }^{\circ}\text{C}$ and from $310\text{ }^{\circ}\text{C}$ to $515\text{ }^{\circ}\text{C}$. The initial peak results from the deterioration of oil, plasticizers, and additives within the tire, whereas the subsequent peak signifies the decomposition of natural rubber, polybutadiene, and styrene butadiene. Arias *et al.*³⁴ indicated that TGA analysis of waste tires demonstrates that the most significant mass loss occurs between 200 and $550\text{ }^{\circ}\text{C}$, especially at heating rates from 5 to $20\text{ }^{\circ}\text{C per minute}$. This indicates that within this temperature range, most organic constituents of the tire experience considerable thermal degradation, leading to significant mass loss. Betancur *et al.*³⁵ categorized the thermal degradation process of waste tires into three primary zones according to temperature ranges. The initial zone, ranging from 100 to $270\text{ }^{\circ}\text{C}$, pertains to water's evaporation and additives' preliminary degradation. The second zone, ranging from 270 to $350\text{ }^{\circ}\text{C}$, indicates the degradation of natural rubber (NR). The third zone, ranging from 350 to $450\text{ }^{\circ}\text{C}$, is marked by the cleavage of disulfide bonds (S-S), indicative of the degradation of synthetic rubber varieties like styrene-butadiene. Upon reaching a temperature of $550\text{ }^{\circ}\text{C}$, the pyrolysis process is typically deemed complete, as no substantial mass loss is observed thereafter.



The weight reduction during the thermal degradation of the CS100WT0 specimens can be categorized into three phases. The initial phase entails a weight reduction of 7.18% attributed to water evaporation, aligning with Defo *et al.*³⁶ observations, documenting a biomass weight loss from water evaporation between 7 and 10%. This water is absorbed by cellulose and hemicellulose, which are hydrophilic because of their elevated hydroxyl group content. During the second stage, weight loss transpires due to cellulose and hemicellulose degradation, commencing at a temperature of 258 °C, resulting in a weight drop of 28.89%. The third stage entails lignin degradation, leading to a weight reduction of 49.93% at 326 °C. Defo *et al.*³⁶ observed that coconut shell typically demonstrates the most significant weight loss during this phase, attributable to its elevated lignin content. The remaining weight of the specimen post-degradation is 17.38%. Research conducted by Nadzri *et al.*³⁷ demonstrates that hemicellulose degradation transpires at temperatures ranging from 200 to 350 °C, followed by lignin and cellulose degradation within the 350 to 400 °C range. Additionally, Waters *et al.*³⁸ and El-Sayed *et al.*³⁹ indicated that hemicellulose, cellulose, and lignin decompose at varying temperatures. Hemicellulose typically degrades at lower temperatures (220–300 °C) than cellulose (300–340 °C), and lignin degrades over a greater temperature range (300–900 °C).

The CS75WT25, CS50WT50, and CS25WT75 specimens experienced a mass reduction of 5.73%, 4%, and 2.84% due to water evaporation during the initial phase. This study demonstrates that an increased coconut shell content correlates with a greater mass reduction in the specimens resulting from water evaporation. This effect can be ascribed to the elevated water content in coconut shells relative to waste tires, particularly when the coconut shells have not undergone rigorous drying. The increased water content makes more water molecules accessible for evaporation during heating. Coconut shells possess a greater surface area per unit mass than waste tires. An increased surface area enhances air exposure, expediting the evaporation process. Incorporating old tires diminishes the effective surface area exposed to the atmosphere, reducing the evaporation rate.^{40,41} After the initial phase, the second phase is marked by a swift alteration in mass. The mass reduction in the second phase for CS75WT25, CS50WT50, and CS25WT75 was 77.54%, 70.08%, and 59.76%, respectively. The mass reduction in the second phase transpired at 264 °C for CS75WT25, 268 °C for CS50WT50, and 290 °C for CS25WT75.

The increase in temperature during this phase (about 200 °C to 450 °C) indicates that the waste tire (WT) component requires greater activation energy for breakdown compared to pure coconut shell (CS). This suggests that the incorporation of WT diminishes the overall thermal reactivity of the combination. Nonetheless, incorporating WT can delay combustion, necessitating elevated temperatures for complete breakdown.⁴² This study's findings align with the research by Yin *et al.*,⁴² which showed that goat manure (GM) has a quicker peak decomposition rate and greater mass loss than used tires (WT). In contrast, the intricate structure of WT diminishes heat transfer efficiency, leading to increased energy demands and higher peak temperatures.

In addition, the residual mass in the specimens was 15.87%, 25.03%, and 37.4% for CS75WT25, CS50WT50, and CS25WT75, respectively. Meanwhile, the residual mass in the CS100WT0 and CS0WT100 specimens was recorded at 17.38% and 33.94%. The study's findings indicate that enhancing the waste tire content results in a rise in temperature during the second phase. Furthermore, the mass reduction in the second phase diminishes as the concentration of waste tires rises. The residual material in the specimens similarly rises with the increasing concentration of waste tires. Waste tires comprise a substantial quantity of inorganic, non-biodegradable compounds, including carbon black and metals.^{43,44} These components remain unbroken during thermal degradation, resulting in an accumulation of residual material. Moreover, using metals in tire compounds affects the thermal degradation and leads to a greater quantity of residue post-degradation. The findings align with the research by Yaghi *et al.*,⁴⁵ which indicates that pure used tires (WT) demonstrate superior thermal stability. The analysis showed that substantial weight loss initiates at approximately 350 °C, continuing with consistent decomposition until it concludes at 500 °C, signifying the degradation of elastomeric compounds in the tires. Additionally, WT exhibited a significant quantity of residue at elevated temperatures, indicating the presence of carbon black and non-volatile compounds that withstand thermal degradation, even under high-temperature conditions.

In this study, Thermogravimetric Analysis (TGA) underscores the significance of optimizing the trade-off in the use of Coconut Shell (CS) and Waste Tire (WT) as potential renewable energy sources. The CS and WT ingredients can be optimized in fuel blends to leverage CS's high reactivity for efficient ignition,⁴⁶ while also utilizing the energy potential inherent in WT. Limiting the concentration of WT is essential for maintaining the overall reactivity of the blend and minimizing the ash fraction, which is critical for thermal efficiency and the operational feasibility of the energy conversion system.

Fig. 4 illustrates the outcomes of the DTG (Derivative Thermal Gravimetric) testing conducted in this investigation.

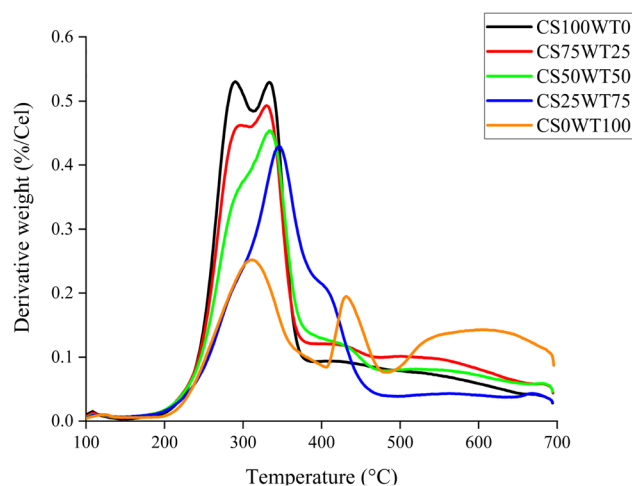


Fig. 4 DTG test results for each specimen.



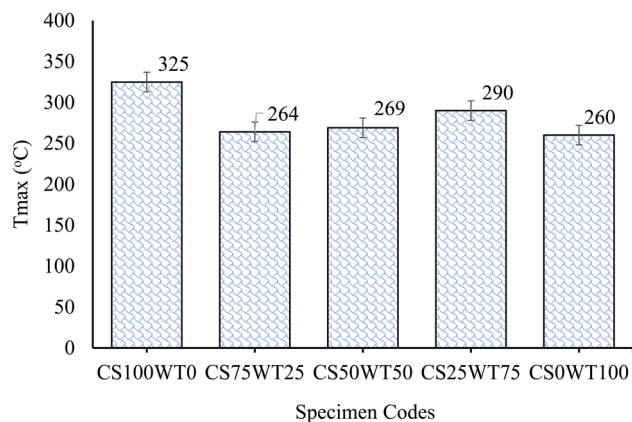


Fig. 5 Comparison of T_{max} in each specimen.

Specimens CS100WT0, CS75WT25, CS50WT50, CS25WT75, and CS0WT100 produce T_{max} (°C) values of 325, 264, 269, 290, and 260, respectively. Fig. 5 shows the comparison of T_{max} generated in each specimen. The test results indicate that the specimen with a 100% coconut shell composition has the maximum T_{max} . This suggests that the primary components of coconut shells, including cellulose, hemicellulose, and lignin, exhibit superior thermal stability compared to the components of waste tires. This implies that the components of coconut shells necessitate elevated temperatures to undergo substantial decomposition. In the meantime, the specimen with a 100% composition of waste tires exhibited the lowest T_{max} . This is because the components of waste tires, including synthetic rubber, additives, and fillers, decompose at temperatures that are lower than those of coconut shells.^{47,48}

The blending of waste tires and coconut shells results in a significant reduction in T_{max} . The results of this study demonstrate that specimens composed entirely of waste tires and those incorporating waste tires exhibit a lower T_{max} compared to specimens made solely from coconut shells. This observation indicates that the decomposition of specimens comprising a waste tire blend and those composed entirely of waste tires occurs at a lower temperature than that of specimens made from 100% coconut shells. The T_{max} value increases with a higher proportion of waste tires in specimens composed of a mixture of coconut shells and waste tires. The phenomenon is evident in specimens CS75WT25, CS50WT50, and CS25WT75, which exhibit an increase in T_{max} as the concentration of waste tires increases. The thermal degradation process becomes more complex as the concentration of waste tires increases, which may lead to higher T_{max} values. This is ascribed to the augmented thermal mass and the inclusion of diverse additives and rubber varieties that break down at varying temperatures. Moreover, the cleavage of bonds and ensuing reactions of tire components, including polyisoprene rubber (IR) and styrene-butadiene rubber (SBR), lead to an elevation in T_{max} as the concentration of waste tires increases.^{49,50} Maximum decomposition is a critical metric for evaluating the thermal stability of a material, as it represents the maximum mass loss in a specimen that occurs at a specific temperature (T_{max}). The

thermal stability of the specimen is enhanced by a higher T_{max} .^{29,51–53} In this study, the Derivative Thermogravimetric Analysis (DTG) demonstrates an interaction in a blend of waste tire (WT) with a low proportion, which is characterized by an impressive rise in thermal reactivity at lower temperatures. The observed enhanced reactivity, indicated by the shift of the maximum temperature (T_{max}) to a lower value, is attributed to the catalytic action of mineral components, including ZnO and sulfur, present in the WT ash. This action effectively reduces the energy required for the decomposition of biomass, specifically coconut shell (CS). In contrast, the decomposition profile is progressively shifted to higher temperature ranges (>450 °C) as the WT proportion increases, as evidenced by the enlargement and prolongation of the decomposition area. This phenomenon indicates the predominance of the intrinsic thermal stability of rubber and carbon black components in WT, which exhibit resistance to degradation. Consequently, elevated operating temperatures are necessary to achieve complete burnout in the WT-rich blend, which tends to decelerate due to carbon black residue.

Pan *et al.*²⁷ indicate that the incorporation of tire powder into coal substantially influences its combustion characteristics. The ignition temperatures for samples with 10%, 20%, and 40% tire powder were recorded at 424.11 °C, 410.86 °C, and 370.69 °C, respectively. These data indicate that the ignition temperature reduced by 9.34 °C, 22.59 °C, and 62.76 °C for 10%, 20%, and 40% tire powder blends, respectively. The high volatile content of tire powder, which rapidly evaporates and ignites at lower temperatures, reduced the ignition temperature due to its presence.

Fig. 6 illustrates the results of the Fourier Transform Infrared Spectroscopy (FTIR) test conducted in this study. This investigation utilized the wavenumber range of 400 to 4000 cm^{-1} for FTIR testing. FTIR testing is typically employed to ascertain the functional groups in a material. This analysis also identifies specific functional groups and molecules, as well as chemical structures and compositions that can be converted into products. The results of this test can be employed to gain a comprehensive understanding of the chemical structure of a material. Most biomass materials, including coconut shells, generally contain similar functional groups, including alcohols, carboxyl groups, phenols, aldehydes, ketones, and ethers.

A maximal broadening is observed at a wavenumber of 3408 cm^{-1} in CS100WT0 (100% coconut shells). Because of the extensive hydrogen bonding of cellulose, this suggests the presence of hydroxyl group bonds (H_2O). The peak at 2931 cm^{-1} indicates CH's elongation, which generates vibrations in the CH, CH_2 , and CH_3 groups. The peak indicates the presence of C=C in the aromatic ring at 1742 cm^{-1} . The significant changes in C–O carboxyl in the wavenumber range of 1608 cm^{-1} to 1255 cm^{-1} are interpreted because of the activity of carboxyl-oxygen atoms, which induces changes in the region. The peak observed in the 1161–1050 cm^{-1} wavenumber range suggests the presence of silica, which in turn indicates the presence of bending and stretching vibrations on Si–O.⁵⁴

As documented by Liyanage and Pieris,⁵⁵ the Fourier Transform Infrared (FTIR) examination of coconut shell definitively



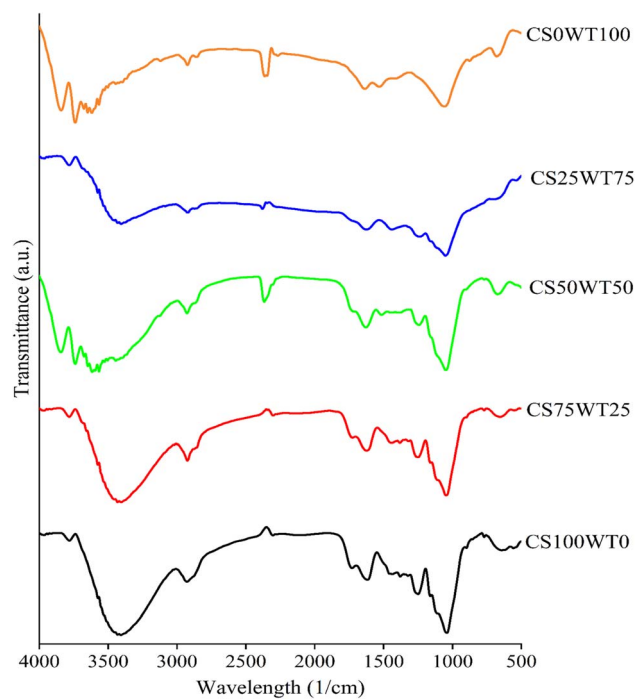


Fig. 6 FTIR test results for each specimen.

established that the substance is lignocellulosic, predominantly cellulose, hemicellulose, and lignin. The components were found by detecting particular functional groups. The FTIR spectrum exhibited a prominent -OH stretching peak ranging from 3357 to 3650 cm^{-1} , indicating significant hydrogen bonding in cellulose. A C=O stretching peak showed the presence of hemicellulose at 1735 cm^{-1} , whilst the aliphatic C-H vibration was notably observed at 2921 cm^{-1} . The structural characteristics of lignin were evidenced by two aromatic C=C stretching peaks at 1685 cm^{-1} and 1638 cm^{-1} , together with phenolic C-O vibrations at 1246 cm^{-1} and 1239 cm^{-1} .

The stretching vibration of C-H on the CH_3 functional group was indicated by a peak at a wavenumber of nearly 2900 cm^{-1} in the FTIR test results of CS0WT100 (100% waste tires). The peaks at 1640 cm^{-1} and 1524 cm^{-1} suggest the presence of C=C vibrations in waste tires. The peaks at 1450 cm^{-1} and 1045 cm^{-1} , respectively, suggest C-O-C stretching. The peak at a wavenumber of 665 cm^{-1} indicates the presence of C-S vibration in waste tires.⁵⁶ The findings of this investigation demonstrate that the peak intensity is induced by the inclusion of waste tires in each specimen, which suggests the presence of O-H functional groups and Si-O stretching and bending vibrations. This is evident at wavenumbers 3408 cm^{-1} and $1161\text{--}1050\text{ cm}^{-1}$. The spectrum of CS100WT0 exhibits a pronounced and extensive absorption in the range of $3600\text{--}3200\text{ cm}^{-1}$, corresponding to O-H stretching, along with a distinct peak at $1250\text{--}1000\text{ cm}^{-1}$, indicative of C-O stretching. These data indicate a high content of high hydroxyl groups, cellulose, and hemicellulose in the sample. The TGA and DTG results substantiate this interpretation, indicating high initial reactivity and considerable mass loss at elevated temperatures,

which signifies the thermal degradation of polysaccharide components. In addition, CS100WT0 exhibits the maximum water evaporation during the initial phase of the TGA test.

Conversely, CS0WT100 exhibits a significant reduction in the intensity of the O-H and C-O peaks relative to CS100WT0. The sample exhibits significant absorption features within the $1600\text{--}1450\text{ cm}^{-1}$ range, indicative of C=C stretching, and the $3000\text{--}2800\text{ cm}^{-1}$ range, associated with C-H aliphatic stretching. The absorptions support the conclusion that CS0WT100 is primarily characterized by stable polymer structures, including aromatic carbon, aliphatic carbon, and inert solids such as carbon black and residual rubber fractions. The findings corroborate the TGA results, demonstrating enhanced thermal stability and a higher residue quantity in specimens with elevated waste tire content. This phenomenon is due to the significantly greater resistance of the C=C aromatic bonds to thermal degradation and bond fragmentation. Nevertheless, the combination of waste tires with each specimen led to a lower rate of water evaporation than the specimen made entirely of coconut shells. Furthermore, the presence of CH stretching in the CH , CH_2 , and CH_3 groups is indicated by the attenuation of the peak at the wavenumber 2931 cm^{-1} , which is also a result of the addition of waste tires. Organic compounds, including the primary components of coconut shells, such as cellulose, hemicellulose, and lignin, are rich in C-H bonds.⁵⁷

The presence of elastomeric components such as talc, carbon black, and silica in used tires can influence the FTIR spectrum of the mixture of waste tires and coconut shell. These compounds can cause peak shifts and reduce the intensity of characteristic peaks, particularly the O-H peak at a wavelength of around 3400 cm^{-1} . An increase in the concentration of waste tires in the sample can lead to a reduction or complete disappearance of the O-H peak. The presence of certain additives and modifiers in used tire material can interact with hydroxyl groups, causing a decrease in O-H peak intensity. This indicates that an increase in waste tire concentration in the specimen correlates with a decrease in bound water content in the material, as evidenced by a decrease in absorption intensity at wavelengths around 3400 cm^{-1} .

The FTIR test results in this study are consistent with the findings of Khan *et al.*⁵⁸ Their study of pyrolysis products showed that the addition of waste tires significantly reduced the appearance of O-H groups in the samples, indicating a characteristic transition from polar (rice straw) to non-polar (used tires). As the concentration of used tires increases, the absorption intensity of the O-H group ($\sim 3400\text{ cm}^{-1}$) decreases. Additionally, Khan *et al.*⁵⁹ found that the intensity of O-H group absorption ($\sim 3400\text{ cm}^{-1}$) was lower in the 50 : 50 coal and used tire mixture compared to the 70 : 30 coal and used tire mixture. This indicates that an increase in the amount of waste tires correlates with a decrease in moisture content in the resulting specimens.

The X-ray diffraction (XRD) testing findings from this study are shown in Fig. 7. X-ray diffraction (XRD) examination was conducted to determine the generated phases. X-ray diffraction (XRD) observations were conducted at angles ranging from 10 to 80° , with a step rate of 0.2 . The primary diffraction peaks



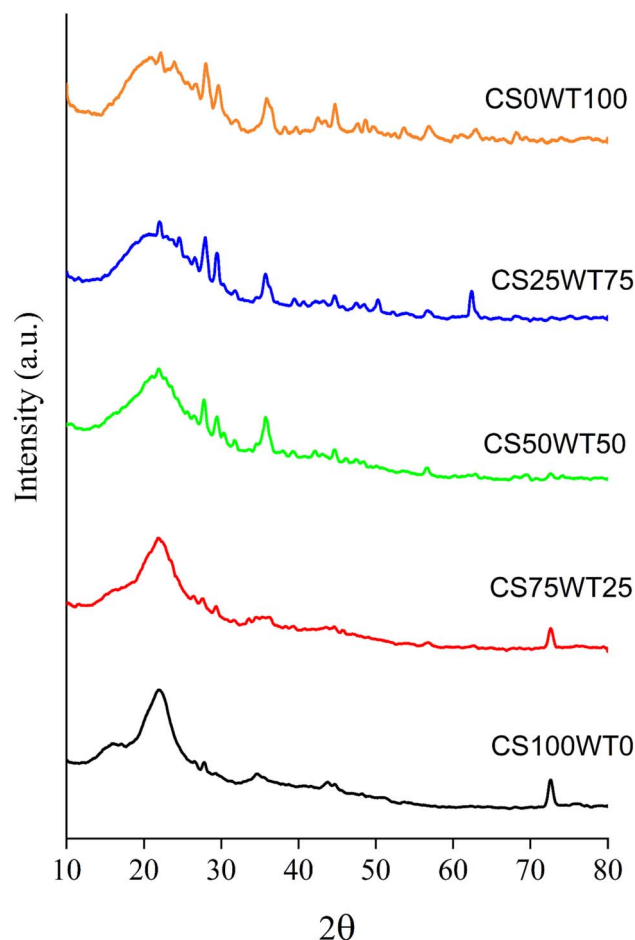


Fig. 7 XRD test results for each specimen.

detected in CS100WT0 containing 100% coconut shells are at 15.33° , 22.03° , 34.65° , and 72.69° , corresponding to cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), quartz (SiO_2), moissanite (SiC), and cristobalite (SiO_2) respectively. The identification of cordierite, quartz, moissanite, and cristobalite was achieved by correlating the measured diffraction patterns with the relevant references in the International Center for Diffraction Data—Powder Diffraction File (ICDD PDF): 82-1541,⁶⁰ 82-0512,⁶⁰ 73-1708,⁶¹ and 01-082-0512.⁶² Quartz has the maximum intensity among these peaks.^{63,64}

The X-ray diffraction (XRD) analysis of CS0WT100, consisting entirely of waste tire, revealed peaks corresponding to natural rubber, styrene-butadiene rubber (SBR), and carbon black used as filler.

Furthermore, the waste tire also contained additional contaminants, as evidenced by the peaks of zinc oxide and nitrogen and a minor value for silica. The presence of the SBR material is indicated by the broadening peak observed at $2\theta = 20^\circ$.⁶⁵ Conversely, the natural rubber material was detected at 2θ peaks within the 13 to 24° range. Peaks observed at 2θ within the range of 36 to 37.73° suggest the presence of ZnO. Zinc oxide (ZnO) is used in tires to activate vulcanization. Meanwhile, the presence of ZnS is indicated by peaks with modest intensity at $2\theta = 28, 47.83$, and 56° . The peaks at approximately around $2\theta =$

24 and 44° correspond to the carbon black structure employed as a filler within the waste tire structure.^{66,67} Conversely, the peak at around $2\theta = 32$ and 39° corresponds to the CuO structure in the waste tire structure.^{68,69} The presence of CuO was subsequently identified with ICDD card Number. 00-045-0937.⁶⁸ Khodair *et al.*⁶⁹ conducted an XRD examination of pure CuO, revealing prominent peaks at $2\theta = 32.6652^\circ$, 35.7253° , and 38.9214° . These findings correspond with the research of Khan Zahir Ahmed and Mohammad Faizan.⁷⁰ The X-ray diffraction (XRD) analysis of used tires revealed a predominant peak at $2\theta = 13.03^\circ$, indicative of amorphous natural rubber. A slight peak at $2\theta = 23.07^\circ$ was ascribed to synthetic rubber. Zinc oxide (ZnO) was identified by two weak reflections at $2\theta = 35.02^\circ$ and $2\theta = 56.41^\circ$, while a reflection at $2\theta = 47.38^\circ$ indicated the presence of zinc sulfide (ZnS). Amorphous organics and carbon black were evidenced by the broadening of the diffraction profile in the 2θ range of 10 – 20° . The X-ray diffraction (XRD) analysis conducted by Dziejarski *et al.*⁶⁶ on recovered carbon black indicated a peak at $2\theta = 24.83^\circ$, commonly associated with graphite. Lazzarini *et al.*⁶⁷ reported that the crystal structure of graphite is identifiable by the presence of two peaks at approximately $2\theta = 44^\circ$ and 80° .

The findings of this investigation indicate that the tire in question comprises natural rubber, SBR, ZnO, ZnS, carbon, and CuO composites. The inclusion of waste tires in the specimen results in a reduction in the strength of the peaks of quartz and cristobalite. Once the residual content of used tires approaches 50%, the peaks corresponding to cristobalite and cordierite disappear. Concurrently, the intensity of the quartz peak also decreases.^{70–72}

The analysis of the calorific values of the specimens acquired in this study is depicted in Fig. 8. The specimens CS100WT0, CS75WT25, CS50WT50, CS25WT75, and CS0WT100 had calorific values (MJ kg^{-1}) of 27.01, 27.31, 27.62, 27.81, and 27.75, respectively. Overall, the calorific values of the five samples exhibit a tendency to rise from CS100WT0 to CS25WT75, followed by a smaller decrease in CS0WT100. The findings of this investigation indicate that CS25WT75 exhibits the highest calorific value, whilst CS100WT0 records the lowest calorific value. This phenomenon is attributed to the lower OH peak intensity observed in CS25WT75, as determined by FTIR

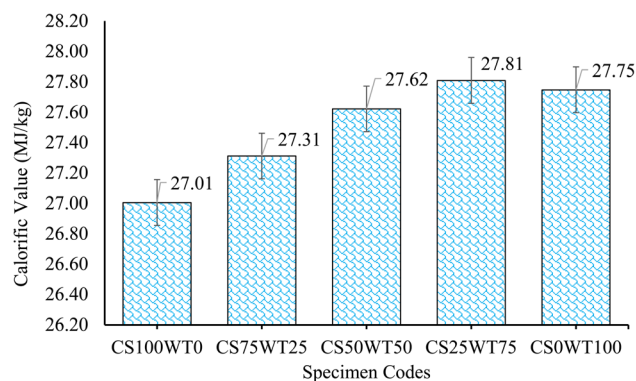


Fig. 8 The comparison of the calorific values of all specimens.



analyses. This indicates that the water content in CS25WT75 is decreasing. At decreased water content, greater energy generation is possible due to the reduced energy required for water evaporation. Lower water content corresponds to higher calorific values.^{57,73–75} This contrasts with CS100WT0, which has a distinct and intense OH peak. The energy necessary to evaporate the water content in CS100WT0 is greater, and the calorific value produced is lower.

This study introduces the utilization of waste tires as an innovative approach to waste management and the development of sustainable recycling practices. Previous studies have examined the utilization of waste tires in various forms, such as granulated tires, whole tires, and shredded tires, exhibiting distinct physical and chemical characteristics suited to specific applications.^{76–78} Waste tires are known to have high calorific value (over 29 MJ kg⁻¹) due to their hydrocarbon content, which is similar to that of fossil fuels.^{27,79–81} Cao *et al.* reported that waste tires comprise over 90% organic material, notable for their high carbon content and calorific value surpassing those of coal.⁸² As a result, waste tires are an extremely high-calorie fuel source.^{76,82,83} This makes them an excellent alternative fuel source for power plants, lime production, steel mills, cement factories, and paper mills.^{76,84} Utilizing waste tires as a fuel source mitigates environmental issues associated with accumulating non-biodegradable waste tire, diminishes dependence on conventional fossil fuels, and lowers energy costs for enterprises.^{27,79–81}

Table 2 presents a comparison of calorific values between the used tire–coconut shell mixture and the reference solid fuels. The study's findings indicate that the specimens produced demonstrate elevated calorific values, varying from 27.01 to 27.81 MJ kg⁻¹. These values substantially exceed those of numerous traditional solid fuels. Sutapa *et al.*⁸⁵ indicated that Calliandra wood (*Calliandra calothyrsus*) possesses a calorific

value of 19.25 MJ kg⁻¹, while M. M. Hoque and S. C. Bhattacharya⁸⁶ determined that coconut shell has a calorific value of 18.32 MJ kg⁻¹. Additionally, Ahmad *et al.*⁵⁴ demonstrated that the calorific values of various biomass types exhibit a wide range, with palm kernel shell exhibiting the highest value (20.40 MJ kg⁻¹) and rice husk the lowest (13.80 MJ kg⁻¹). The calorific values of various reference fuels, including coal (16.2 MJ kg⁻¹), coconut shells (19.4 MJ kg⁻¹), bagasse (16.9 MJ kg⁻¹), hardwood (18.8 MJ kg⁻¹), and wood (15.9 MJ kg⁻¹), are generally lower than those presented in this study.

H. Liu⁸⁷ revealed that solid fuels from wood, grass, rice straw, and coal possess calorific values of 6–18 MJ kg⁻¹, 4 MJ kg⁻¹, 5 MJ kg⁻¹, and 27.99 MJ kg⁻¹, respectively. The research conducted by Farooq *et al.*⁸⁸ demonstrates that enhancing the concentration of waste tires in a fuel blend with wheat straw significantly improves the calorific value of the blend, with values rising from 23.3 to 40.7 MJ kg⁻¹. Rikmann *et al.*⁸⁹ demonstrated that incorporating low-quality recycled carbon black (rCB) derived from the pyrolysis of waste tires into peat residue markedly enhanced the calorific value of the resulting blend. The calorific value of pure peat residue, initially measured at 14.5 MJ kg⁻¹, increased by 45% to 21.0 MJ kg⁻¹ upon incorporating 10 wt% rCB. The study indicated that excessively high concentrations of rCB may lead to incomplete carbon combustion, consequently elevating the proportion of unburned residue within the ash substance.⁸⁹

The calorific values of the specimens in this investigation exceed the full spectrum of natural biomass fuels and approximate those of coal, suggesting significant potential for these blends to be developed as viable alternative energy sources. An elevated calorific value indicates an increased energy yield per unit mass, improving combustion efficiency and minimizing the material needed to generate an equivalent energy output. This attribute is vital for the practical application of sustainable energy production systems.^{90,91}

Utilizing waste tire and coconut shell blends as alternative fuels presents considerable potential and provides various environmental advantages. Waste tires, classified as non-degradable solid waste, pose significant pollution risks if not managed appropriately. Thermochemical methods, including pyrolysis and gasification, enable the conversion of waste tires into liquid fuel and activated carbon residue, facilitating reuse.^{92,93} Coconut shells, classified as agricultural biomass waste, can be transformed into bio-oil and biochar, with significant economic value. Using these two waste types as alternative energy sources reduces solid waste volume and may decrease pollutant emissions relative to fossil fuel combustion.^{94–96} Research indicates that co-pyrolysis of waste tires and biomass produces renewable energy with markedly reduced emissions, thus presenting a more environmentally sustainable option. The activated carbon residue from this mixture has demonstrated efficacy in capturing carbon dioxide and other pollutants, aiding climate change mitigation efforts.^{94–96} The conversion of waste into fuel generates economic opportunities and aligns with circular economic principles by prolonging material lifecycles and decreasing reliance on primary natural resources.^{97,98}

Table 2 Comparison of the calorific values of waste tire–coconut shell blends and reference solid fuels

Specimen/biomass	Calorific value (MJ kg ⁻¹)	References
CS100WT0	27.01	Current study
CS75WT25	27.31	
CS50WT50	27.62	
CS25WT75	27.81	
CS0WT100	27.75	
Coal	16.2, 27.99	54 and 87
Palm kernel shell	20.4	54
Coconut shell	18.32, 19.4	54 and 87
Calliandra wood	19.25	85
Hardwood	18.8	54
Wood	15.9, 6–18	54 and 87
Bagasse	16.9	54
Rice husk	13.8	54
Rice straw	5	87
Grass	4	87
Wheat straw (WS)	23.3	88
Waste tire (WT)	41.3	88
WS/WT 2 : 3	40.7	88
Recycled carbon black (10 wt%)/peat	21	89



The present study has successfully evaluated the thermogravimetric and physicochemical properties of the waste tire-coconut shell blend. However, further research is necessary to investigate its potential as an alternative fuel. The need for additional research is highlighted by the study's shortcomings, which include the lack of emission analysis, the use of a single heating rate in the TGA testing, and the limited ratio of coconut shell to waste tire blend. Emission analysis is essential for assessing the environmental effects of the combustion process of this fuel blend. Moreover, performing TGA tests at different heating rates is necessary to analyze the material's thermal properties under varying conditions comprehensively. Ultimately, broadening the spectrum of mixing ratios will provide significant insights into the alterations in the fuel's qualities resulting from different amounts of coconut shell and waste tire blends.

4 Conclusions

This study has effectively described the thermogravimetric and physicochemical properties of the waste tire and coconut shell blend. Based on TGA analysis, the residue mass for CS100WT0, CS75WT25, CS50WT50, CS25WT75, and CS0WT100 specimens is 17.38%, 15.87%, 25.03%, 37.4%, and 33.94%, respectively. The higher waste tire content increases the production of residue for specimens such as CS75WT25, CS50WT50, and CS25WT75. This phenomenon is attributable to the inorganic constituents of waste tires, including carbon black and metals, which are non-biodegradable and remain during thermal degradation. Conversely, DTG testing reveals T_{\max} values for the CS100WT0, CS75WT25, CS50WT50, CS25WT75, and CS0WT100 specimens of 325 °C, 264 °C, 269 °C, 290 °C, and 260 °C, respectively. The CS100WT0 specimen exhibits the maximum T_{\max} of 325 °C, signifying the superior thermal stability of the material it encompasses. In contrast, the CS0WT100 specimen exhibits the lowest T_{\max} of 260 °C, indicating that the waste tire constituents decompose at a lower temperature than the coconut shell constituents. The augmentation of waste tire content in the mixture results in a diminution of T_{\max} , signifying a decline in the thermal stability of the blend.

The predominant crystal phase in coconut shells is quartz, followed by cordierite and cristobalite. Crystalline phases are present in synthetic rubber in waste tires, including SBR (styrene-butadiene rubber), fillers such as carbon black, and additives such as zinc oxide (ZnO) and zinc sulphide (ZnS). As the proportion of waste tires increases, the peak intensity of the quartz, cordierite, cristobalite, and moissanite phases decreases. This work demonstrates that adding waste tires to each sample leads to peak intensity, suggesting O–H functional groups and stretching and bending vibrations on Si–O. This phenomenon is prominently observed at wavenumbers of 3408 cm^{-1} and 1161–1050 cm^{-1} .

The specimens CS100WT0, CS75WT25, CS50WT50, CS25WT75, and CS0WT100 had calorific values (MJ kg^{-1}) of 27.01, 27.31, 27.62, 27.81, and 27.75, respectively. The specimen containing 75% waste tires and 25% coconut shells (CS25WT75) had the greatest calorific value, indicating its potential as an

effective combustion fuel. Coconut shells, with their exceptional thermal stability and a higher saturation of fixed carbon, can prolong the combustion period, whilst waste tires offer a more substantial increase in energy. The elevated calorific value of CS25WT75 (27.81 MJ kg^{-1}) is comparable to that of coal (16.2–27.99 MJ kg^{-1}), rendering it suitable for co-firing in steam power plants or industrial applications like cement and steel production. This blend can reduce coal consumption, decrease CO_2 emissions, and minimize total fuel production expenses. Moreover, CS25WT75 can serve as a feedstock for pyrolysis, yielding bio-oil, charcoal, and synthetic gas. Applications of pyrolysis utilizing this mixture generate renewable energy with markedly reduced emissions, rendering it a more ecologically sustainable option. However, limiting the concentration of waste tires is essential for maintaining the overall reactivity of the blend and minimizing the ash fraction, which is critical for thermal efficiency and the operational feasibility of the energy conversion system. This research significantly contributes to advancing sustainable energy solutions that diminish reliance on fossil fuels and improve waste management. The research aligns with multiple United Nations Sustainable Development Goals (SDGs), specifically Goal 7 (Affordable and Clean Energy) and Goal 12 (Responsible Consumption and Production).

Author contributions

The authors confirm their contributions to the paper as follows: Samsudin Anis and Sukarni Sukarni: methodology, formal analysis, and conceptualization; Sivasubramanian Palanisamy and Ahmad Indra Siswantara: writing – review & editing, methodology, and formal analysis; Sonika Maulana, Deni Fajar Fitriyana, Adhi Kusumastuti and Januar Parlaungan Siregar: validation, formal analysis, and data curation; Alavudeen Azeez, Aravindhan Alagarsamy and Mohamed Abbas: writing – review & editing, validation, investigation, formal analysis, and conceptualization; Shaen Kalathil and Mezigebe Belay: administration, funding, validation, and investigation. The authors read and approved the final manuscript.

Conflicts of interest

The authors declare no conflicts of interest to report regarding the present study.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

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