

## Prospective energy content assessment of waste biomass and polymer via preliminary analysis

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### ARTICLE INFO

#### Keywords:

Dulong formula  
Vandralek  
Biomass waste  
Ultimate and proximate analysis  
Thermogravimetric analysis (TGA)  
Energy content

### ABSTRACT

Energy generation from waste biomass offers a promising solution for reducing greenhouse gas emissions and promoting a circular economy. This study investigates the energy potential of various organic materials, including rice husk, soybean, lemon myrtle, waste coffee ground, and empty fruit bunch, co-pyrolysed with HDPE at 500 °C and 50:50 blending ratio for 1 h. Proximate, ultimate, and thermogravimetric analyses were conducted up to 700 °C to determine elemental composition and thermal behaviour. Dulong's formula, modified Dulong's formula, and Vandralek's equation were utilised to assess energy content. Proximate analysis revealed rice husk as the highest in volatile matter (73.08 %), while waste coffee ground had the lowest (32.0 %), and HDPE showed 89.90 %. Ultimate analysis showed organic waste carbon ranges from 25.59 % to 48.75 %, and HDPE at 82.24 %. Pyrolysis reactions yielded distinct distributions of bio-oil, char, and gas, with empty fruit bunch producing the highest oil percentage (26.49 %), lemon myrtle yielding the highest gas (31.07 %), and waste coffee ground favouring char production (74.89 %). Discrepancies in heating values were observed, with Dulong's formula underestimating values for rice husk, soybean, and waste coffee ground (−10 % to −35 %) and slightly overestimating for lemon myrtle, empty fruit bunch, and HDPE (1 %–25 %). The modified Dulong formula accentuated underestimations, particularly for soybean (−451 %). The Vandralek formula showed positive error ranges (8 %) for biomass samples but underestimated HDPE. This study underscores biomass and HDPE as viable alternatives to conventional energy sources and suggests avenues for future research while highlighting environmental benefits.

### 1. Introduction

The historical trajectory of global industrial revolutions propelled by fossil fuels has undeniably catalysed economic, technological, and societal advancements [1]. Currently, the excessive exploitation of crude oil has escalated carbon emissions owing to unregulated oil refining processes and fuel combustion for energy generation. Thus, it is imperative to counteract this impending climate crisis compels a shift towards sustainable energy alternatives [2,3]. Simultaneously, the escalating awareness among global citizens regarding the environmental repercussions of non-renewable energy sources underscores the urgency of steering towards a seamless energy transition agenda. In this context, the focal point of the energy transition landscape has shifted towards fuel generation from biomass, which is notable for its carbon-neutral attributes and low emissions [4]. Conventional

thermochemical conversion processes applied to biomass yield a spectrum of outcomes, including heat, power, and electricity. Biomass gasification, direct combustion, pyrolysis, fermentation, and anaerobic digestion are key techniques, each resulting in three primary products, namely char, biofuel, and gas, dictated by the chosen valorisation route [5–8]. The primary components of biomass, including cellulose, hemicellulose, and lignin, undergo thermochemical reactions to produce a diverse array of chemicals [9]. Therefore, Nguyen et al. [10] also established that biomass serves as a robust precursor for essential raw chemical materials, such as dimethyl furan, characterised by physicochemical properties analogous to petroleum-based fuels. Intriguingly, distinct biomass sources yield varying product distributions contingent on the specific thermochemical or biological conversion processes employed [11].

Biomass feedstock for energy generation originates primarily from

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<https://doi.org/10.1016/j.rineng.2024.102301>

Received 31 August 2023; Received in revised form 9 May 2024; Accepted 21 May 2024

Available online 23 May 2024

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agricultural waste and forestry resources. Common biomass types utilised for energy assessment include rice husks (RH), corncobs (CC), empty fruit bunches (EFB), rubber wood (RW), sugarcane (SC), soybean (SB), and waste coffee grounds (WCG) [12–14]. For example, a study by Nabila et al. focused on EFB gasification, yielding 22.6 % methane (CH<sub>4</sub>) at a reaction temperature of 550 °C [15]. The study also retrieved 29 % carbon monoxide (CO) and 3.4 % hydrogen gas (H<sub>2</sub>). In a similar vein, Lin et al. [16] leveraged an elevated temperature of 600 °C to achieve 42 % higher H<sub>2</sub> production from RH feedstock via gasification. In a different approach, Andrade et al. [17] effectively transformed WCG into over 90 % biochar at 850 °C with restricted O<sub>2</sub>, showing its potential for superior supercapacitor construction, attributed to its heightened porosity and thermal conductivity. Similarly, Farid et al. [18] opted for EFB carbonisation, attaining 62 % biochar yield at 600 °C. These studies exemplify the diverse applications and potentials of various biomass sources for energy and material production.

Within the realm of biomass thermochemical conversion processes, pyrolysis has emerged as the predominant method because of its capability to generate substantial liquid products, particularly in the form of bio-oil [19]. In the context of pyrolysis, Sun et al. [20] achieved a higher proportion of bio-oil relative to char and gas during soybean residue pyrolysis. This study investigated the influence of temperature on yield and revealed that elevating the temperature from 350 to 600 °C did not considerably enhance bio-oil yield. In contrast, Abu Bakar et al. [21] reported diverging outcomes, where pyrolysing lemon myrtle waste at higher temperatures significantly diminished the bio-oil yield. This highlights the nuanced nature of the pyrolysis conditions for targeted product outcomes. It is crucial to recognise that the distinctive composition of lignocellulosic constituents within biomass significantly influences the distribution of pyrolysis products, further accentuating the intricacies of the process. Furthermore, Prakash et al. [22] presented distinct distributions of oil, char, and gas resulting from the pyrolysis of palm EFB, oil palm waste, palm kernel shell, and oil palm fronds. This study revealed that all oil palm biomass waste materials yielded over 50 % bio-oil, with oil palm waste leading to a maximum oil yield of 59 %. These findings were attributed to variations in the carbon, hydrogen, oxygen, and sulphur contents as well as moisture levels and volatile matter across the different oil palm biomass feedstocks. This observation agrees with the findings of Pathy et al. [23], who substantiated that disparate grass biomass types yield distinct proportions of pyrolysis products. These results collectively underscore the influence of biomass composition on the pyrolysis process and subsequent product yields.

Therefore, enhancing the product output of biomass pyrolysis is achievable through co-pyrolysis, which involves the amalgamation of biomass feedstock with plastic waste. Thus, a comprehensive analysis conducted by multiple researchers that investigated the co-pyrolysis of biomass and plastic, revealed a robust synergy that often yields elevated bio-oil yields [24,25]. This synergy is rooted in the promotion of secondary biomass pyrolysis facilitated by the presence of H<sup>+</sup> donors originating from plastics. Importantly, these reviews advocate the use of nondegradable plastic waste to enhance sustainable waste management practices. Incorporating plastic waste into the pyrolysis feedstock enriches the hydrogen composition, thereby facilitating its subsequent conversion into bio-oil via a hydrogenation mechanism [26]. This strategy demonstrates the potential of harnessing the synergistic interaction between biomass and plastic waste for improved product yields and a more sustainable waste management framework. The coupling of thermogravimetric analysis (TGA) with proximate and ultimate analysis furnishes essential insights to facilitate the determination of the feedstock energy content. TGA serves as an indispensable preliminary analysis, adept at screening and comprehending the thermal attributes of biomass and diverse waste materials, thereby guiding subsequent parameter design for pyrolysis. The thermal degradation dynamics extracted from the TGA data, along with the predicted activation energy, play a paramount role in tailoring appropriate pyrolysis reactions conducive to the attainment of the desired end products [27,28]. This

integrated approach capitalises on the predictive capacity of the TGA data to steer the design and optimisation of pyrolysis processes for improved energy conversion.

The ultimate analysis data encompassing both biomass and plastic compositions serve as the foundation for computing predictive values such as the lower calorific value (LCV), higher calorific value (HCV), lower heating value (LHV), and higher heating value (HHV). For instance, Rashedi et al. [29] calculated the LHV and HHV of biomass pellets derived from five distinct biomass sources to identify the most suitable candidate for biofuel production. Dulong's formula was employed to derive and compare the LHV and HHV values for various biomass sources. Similarly, Kamaruddin et al. [30] adopted a parallel approach, utilising the same formula to simulate HHV and LCV for biomass solid waste intended for use as a solid fuel source in power generation. The resulting simulated HHV and LCV values were subsequently correlated with the experimental data, revealing a robust parallelism.

The Dulong formula, formulated by Dulong during the 19th century, holds significant prominence within the combustion science domain for its utility in estimating fuel calorific values. The formula operates under the assumption of a proper association between oxygen and hydrogen, with surplus hydrogen available for combustion. Empirical assessments have revealed its commendable accuracy, typically within a 1.5 % deviation from actual values, particularly evident in coal evaluations against measurements conducted with an oxygen-bomb calorimeter [31]. However, over time, this formula has undergone refinements to accommodate a broader spectrum of fuel sources. In response to the demand for greater inclusivity, Huang et al. [32] undertook the adaptation of Dulong's formula, resulting in improved accuracy when calculating biomass heating values. This enabled Hosokai et al. [33] to further corroborate this approach, attesting to enhanced accuracy in solid fuel assessments through the utilisation of a modified Dulong formula, substantiated by the incorporation of latent heat considerations. This progression highlights the adaptability and ongoing relevance of the formula in accommodating diverse fuel compositions beyond its original scope. Additionally, alternative formulas, such as the Vandralek equation, have been harnessed for estimating the heating values of biomass. On top of that, Hasan et al. [34] executed calculations using the Vandralek formula to assess the heating values of chinaberry wood as a potential coal substitute. Employing this equation, this study endorsed pinewood over chinaberry wood, attributing superior heating values to the former. These investigations underscore the pivotal role of such formulas in preliminary assessments, aiding in the identification of the optimal feedstock for biofuel production.

Furthermore, the Dulong formula finds application beyond coal assessments, proving adept at estimating combustion heats across diverse products, including plastics and agrochemicals, showcasing commendable predictive accuracy. Despite its simplicity, the formula proves robust, with reliable estimations even for products featuring heteroatoms not initially considered in the databases from which these formulas were derived. However, it is noteworthy that in instances of exceptionally high mass fractions of specific elements or under extreme conditions such as process parameters (Temperature, pressure, etc), the Dulong formula, along with its counterpart, the Vandralek formula, may encounter limitations.

In the realm of waste-to-energy technology and waste valorisation, where the conversion of waste into energy holds importance as a convenient and swift pre-assessment of energy content, the utilisation of formulas such as Dulong and Vandralek assumes a critical role in evaluating the calorific values. These formulas serve as indispensable tools for assessing the feasibility and efficiency of various technologies, including gasification and incineration. By facilitating the estimation of potential energy content within waste materials, they inform decision-making processes concerning energy recovery from waste, thereby fostering sustainable practices in waste management. The juxtaposition of the inherent limitations and advantages of each formula offers a

comprehensive framework for selecting the most appropriate biomass type to achieve the desired outcomes. Guided by this rationale, the present study aims to undertake a comparative analysis of the heating values and energy content among five well-established waste biomass and plastic sources. This study will utilise the Dulong, modified Dulong, and Vandrak formulas, and seek to elucidate the relationship between these formulas and the distribution of yield for each co-pyrolysis product across all biomass and plastic feedstocks. Through this investigation, the study endeavours to shed light on the interplay between formula-derived estimations and experimental findings, incorporating insights from thermogravimetric analysis (TGA) to augment the understanding of waste valorisation processes while investigating the swift and accurate estimation of energy content of each waste.

## 2. Materials and method

The process flow presented in Fig. 1 offers a comprehensive visual representation of the method's progression, highlighting key stages. This structured approach facilitated a systematic study, ensuring a precise comparative analysis between the theoretical and experimental results. Each process is elaborated upon in the following sections.

The biomass feedstock samples, dried empty fruit bunch (EFB) with moisture content <10 wt%, were acquired from a palm oil mill at Dengkil, Selangor. Lemon myrtle (LM) was obtained from a residential neighbourhood in Cyberjaya, Malaysia. Soybean (SB) and coffee grounds (WCG) were purchased from a store, while rice husk (RH) was obtained from paddy fields in Sekinchan, Selangor. High-density polyethylene (HDPE) was obtained from mixed sources.

### 2.1. Preparation of feedstock

For the biomass feedstock, sun drying was initially conducted for several days, followed by further drying in an oven at 110 °C for 24 h to ensure the complete elimination of moisture. Subsequently, the biomass was ground with a propeller grinder and sieved to obtain a 1 mm particle size. The preparation and grinding steps were repeated for all types of organic feedstocks before each experiment to maintain consistency and prevent contamination. High-Density Polyethylene (HDPE) was processed using cryogenic grinding, in which ultra-low cold temperatures were applied to plastics using dry ice. This process made the plastics brittle and easily ground into fine particles without altering their composition or affecting subsequent analysis [35]. The HDPE plastics

were mixed with dry ice on a stainless-steel tray and allowed to sit for a few minutes before being fed into a pulveriser (Pulverisette 19, Fritsch) to achieve a 1 mm particle size.

### 2.2. Physicochemical characterisation

Thermal analysis was conducted to study the behaviour of the organic feedstock and HDPE plastic during thermal decomposition using a thermogravimetric analyser (Mettler Toledo, TGA/SDTA851). Approximately 15 mg of each sample was placed in an alumina crucible. The sample was then subjected to continuous heating from room temperature to 1000 °C at a rate of 10 °C/min under nitrogen gas flow at 100 ml/min.

Ultimate and proximate analyses were also performed, as they provided valuable insights into the chemical composition of the feedstock. Ultimate analysis determines the elemental composition (carbon, hydrogen, nitrogen, sulphur, and oxygen), which helps estimate the energy content and potential yield of valuable products. The proximate analysis evaluates the major components of the feedstock (moisture, volatile matter, fixed carbon, and ash), enabling a better understanding of its behaviour during pyrolysis.

Non-catalytic pyrolysis was conducted in a vertical fluidised bed reactor at a temperature of 500 °C with individual feedstock, and 75 g of each feedstock was inserted into the furnace to facilitate the experiment. Nitrogen gas was continuously flowed at a rate of 10 ft<sup>3</sup>/min for a duration of 1 h. The jacketed electrical furnace, at a height of 720 mm, featured a furnace tube with a diameter of 38 mm. A type-K thermocouple placed at the midsection of the furnace facilitated the temperature monitoring. The reactor was allowed to cool to room temperature and subsequently collected to determine the mass balance of the oil, gas, and solid fractions, as shown below.

The amount of pyrolysis products can be calculated using Equations (1)–(4) [36]:

$$Q_{char} = \frac{W_c}{Z_f} \times 100\% \quad (1)$$

where,  $Q_{char}$  = Yield of char (wt%),  $W_c$  = Mass of char (g),  $Z_f$  = mass of feed (g)

$$B_{bio-oil} = \frac{B_b}{Z_f} \times 100\% \quad (2)$$

where,  $B_{bio-oil}$  = Yield of bio-oil (wt%),  $B_b$  = Mass of bio-oil (g),  $Z_f$  = mass of feed (g)

$$Z_f (wt\%) = \frac{Z_f - W_c}{Z_f} \times 100\% \quad (3)$$

where,  $Z_f$  = conversion of feedstock (wt%),  $Z_f$  = mass of feedstock (g),  $Q_c$  = mass of char (g)

The fraction yield of gas was estimated based on the feedstock and product (liquid oil and solid) weight differences.

$$M_g = Z_f - B_b - Q_c$$

$$M_g = \frac{B_b}{Z_f} \times 100\% \quad (4)$$

where,  $M_g$  = mass of feedstock (g),  $B_b$  = mass of oil (g),  $Q_c$  = theoretical yield of gas (%),  $Z_f$  = mass of feed (g)

### 2.3. Mathematical models

Mathematical models have been used to predict the energy content of different feedstocks [37]. The energy content of each feedstock was calculated and compared using four distinct formulas, all based on the variables derived from the ultimate analysis and expressed as weight percentages. The Dulong and Vandrak formulas operate under the

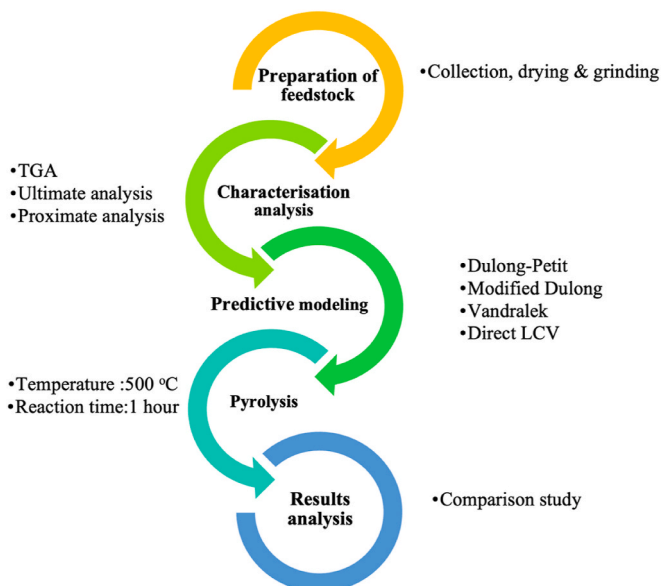


Fig. 1. General process flow for the study.

assumption of ideal combustion conditions, wherein all hydrogen in the fuel reacts with oxygen to produce water vapour (steam). These calculations simplify the estimation process by prioritising the major combustible elements in the fuel as they do not account for the heat released from the condensation of steam during combustion. As a result, steam is typically considered negligible in calorific value calculations [38].

Several distinct differences exist between the Dulong, modified Dulong, Vandralek, and direct LCV calculation methods. The Dulong formula is a classical approach based on elemental composition, assuming ideal combustion conditions. In contrast, the modified Dulong formula adjusts for deviations in hydrogen and oxygen content, enhancing accuracy. The Vandralek formula incorporates additional parameters like carbon content and hydrogen-to-carbon ratio, offering improved precision. Direct LCV calculation bypasses formulas altogether, directly measuring the lower heating value of a fuel sample through calorimetry. Thus, Eq. (5) to Eq. (8) showcases the differences between the mathematical formula as shown in the following:

Dulong formula:

$$HCV = 4.18(78.4C + 241.3H + 22.1S) \quad (5)$$

Modified Dulong:

$$HCV = 4.18 \left[ 78.4C + 241.3 \left( \frac{H}{8} \right) \right] + 22.1S \quad (6)$$

Vandralek:

$$HCV = 4.18 [(85C + 270H) + 22.1(S - O)] \quad (7)$$

Direct formula, LCV:

$$LCV = 4.18(94.19C - 0.5501 - 52.14H) \quad (8)$$

Where.

C: Carbon (wt %)

H: Hydrogen (wt %)

S: Sulphur (wt %)

O: Oxygen (wt %)

The calculation of relative error serves as a critical tool in evaluating the accuracy and reliability of estimations derived from the Dulong and Vandralek formulas for calorific value estimation. By quantifying the disparity between calculated values and experimental measurements, valuable insights into the performance of these formulas are gained. Therefore, comparing relative errors across different formulas enables the identification of the most accurate estimation method, essential for decision-making in scenarios like energy content assessments. This process aids in selecting the most suitable formula for practical applications, ensuring precision and reliability in estimating calorific values, particularly in diverse material and fuel studies within the realm of energy research. Consequently, the relative error analysis as shown in Eq. (9) was developed to enhance the applicability of the models and accuracy of the study.

Relative error, RE:

$$\frac{HCV_T - HCV_A}{HCV_T} \times 100\% \quad (9)$$

Where.

HCV<sub>T</sub>: Theoretical value, (MJ/kJ<sup>-1</sup>)

HCV<sub>A</sub>: Actual value, (MJ/kJ<sup>-1</sup>)

### 3. Results and discussion

#### 3.1. Proximate analysis

Proximate analysis, a widely employed method, offers insights into the composition of organic materials by quantifying the fixed carbon, volatile matter, ash, and moisture. Table 1 presents a comprehensive summary of proximate analyses conducted on various materials, including rice husk (RH), soybean (SB), lemon myrtle (LM), waste coffee grounds (WCG), empty fruit bunches (EFB), and High-Density Polyethylene (HDPE).

The ash content indicates that the inorganic residue remained after complete combustion and ranged from 0.10 % in HDPE to 11.67 % in RH, further indicating the corrosiveness and shelf life of the bio-oil after pyrolysis, which is influenced by the peripheral heating capability of the reactor [39]. Fixed carbon quantifies the remaining carbon in the material after heating in the absence of air and varies between 0.02 % (HDPE) and 43.0 % (WCG), indicating that the feedstock is impervious to physical and chemical degradation [40]. Meanwhile, the moisture content indicated that the water content of the material and SB had the lowest moisture content (5.8 %), whereas WCG had the highest (67.0 %). Kusrini et al. [39], also stated that moisture content also offers a foresight to the heating value and combustion temperature because the high water content in fuel can make it harder to ignite, prolonging the burning process while reducing the combustion rate. However, bio-oil viscosity can compensate for the presence of water, making it a suitable substitute fuel.

The volatile matter, constituting the fraction released as gas or vapour during heating, exhibited values ranging from 32.0 % (WCG) to 89.9 % (HDPE). Volatile matter refers to a section of a sample that transforms into gas or vapour under specific heating conditions. It encapsulates combustible constituents that contribute to the energy release during combustion [41]. This parameter also holds significant importance, as it offers a valuable perspective on the eventual post-pyrolysis yields, given that the vapour fraction produced is condensed into liquid bio-oil. Furthermore, it offers valuable cues about combustion behaviour, reactivity, and overall heating value, making it a key determinant in understanding fuel characteristics and utilisation potential [42].

#### 3.2. Ultimate analysis

Ultimate analysis was used to establish the elemental makeup of the organic materials, as shown in Table 2. The data presented outline the outcomes of the ultimate analysis for the six feedstocks: carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O). Carbon and hydrogen constitute the principal elements within organic materials, whereas nitrogen and sulphur occur in relatively smaller proportions. Oxygen is also inherent in organic substances, although its presence is not factored into the ultimate analysis owing to potential variation based on moisture content.

The ultimate analysis results highlight the distinctive elemental compositions of various feedstocks. For instance, HDPE exhibits a high carbon content (82.24 %) and relatively low hydrogen content (13.90 %), whereas soybeans stand out with a relatively elevated nitrogen content (7.63 %) compared to other feedstocks. The carbon content across all organic feedstocks, including HP, indicates their suitability for

**Table 1**  
Proximate analysis for organic waste and HDPE.

Types	RH	SB	LM	WCG	EFB	HDPE
<b>Ash</b>	11.67	4.7	4.88	0.30	4.90	0.10
<b>Fixed carbon</b>	7.8	19.0	23.98	43.0	15.60	0.02
<b>Moisture content</b>	7.45	5.8	7.41	24.7	13.60	10.00
<b>Volatile matter</b>	73.08	70.5	63.72	32.0	65.90	89.90

**Table 2**  
Ultimate analysis of organic waste and HDPE.

Types	RH	SB	LM	WCG	EFB	HDPE
Carbon	39.88	25.59	45.86	48.75	45.63	82.24
Hydrogen	5.54	8.08	6.34	7.88	6.65	13.90
Nitrogen	0.46	7.63	0.47	1.84	0.43	–
Sulphur	0.48	0.47	0.09	0.14	0.09	0.05
Oxygen <sup>a</sup>	53.64	58.23	47.24	41.49	47.20	3.81

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

catalytic thermochemical conversion via co-pyrolysis, which is consistent with previous findings [43]. The bio-oil derived from these feedstocks displays low SOX and NOX concentrations owing to their minimal sulphur and nitrogen levels, rendering them conducive for environmentally friendly conversion processes.

Table 3 lists the hydrocarbon ratio (H/C) and oxygen/carbon ratio (O/C). SB had the highest H/C ratio (0.32) among the tested feedstocks, whereas RH and LM had the lowest (0.14). HDPE had the lowest O/C ratio of 0.05, whereas SB had the highest (2.28). This observation is an important indicator of the potential Higher Heating Value (HHV) of feedstocks. Lower (O/C) ratios often correspond to higher HHV values owing to the lower calorific value of oxygen relative to carbon, as validated by Merckel et al. [44]. This statement is proven by the values presented in Table 3. However, Leng et al. [45] argued that the (H/C) ratio is influenced by the oxygen content, necessitating low oxygen levels for a high HHV. This underscores the significance of deoxygenation processes in enhancing the bio-oil quality, as advocated by the authors.

### 3.3. Thermogravimetric analysis (TGA)

#### 3.3.1. Rice husks

Rice husks, a renewable and abundant biomass waste, have garnered significant interest for their potential applications in various industries, including biofuel production, construction materials, and agriculture [46]. In the first phase of TGA shown in Fig. 2, a weight loss of 6.76 % was observed at a relatively low temperature of 76.78 °C. This initial weight loss is primarily attributed to the evaporation of surface moisture and volatile organic compounds such as residual water and low-molecular-weight organic compounds present in the rice husk sample. These volatile components tended to evaporate at lower temperatures and contributed to the observed weight loss (see Fig. 2).

In the second phase, a significant dip in the TGA curve occurs at 311.68 °C, corresponding to a weight loss of 24.79 %. This phase signifies the decomposition and combustion of the organic components present in rice husks, such as cellulose, hemicellulose, and other complex organic compounds. Cellulose and hemicellulose are the main polysaccharides present in plant materials and serve as structural components of rice husks. During this phase, elevated temperatures cause the thermal degradation of these organic compounds, resulting in the release of volatile gases and the formation of solid residues. The weight loss observed in this phase represents the breakdown and transformation of the organic components.

In the third phase, further weight loss of 10.61 % was observed, resulting in a residue of 10.61 % at 443.78 °C. This weight loss indicates the decomposition of more thermally stable components present in rice husks, such as lignin and other organic compounds with higher molecular weights [47]. Lignin is a complex polymer that provides structural

**Table 3**  
Ultimate analysis & compound ratio for organic waste and HDPE.

Types	RH	SB	LM	WCG	EFB	HDPE
(H/C) <sup>b</sup>	0.14	0.32	0.14	0.16	0.15	0.17
(O/C) <sup>b</sup>	1.35	2.28	1.03	0.85	1.03	0.05

<sup>b</sup> Calculated by ratio.

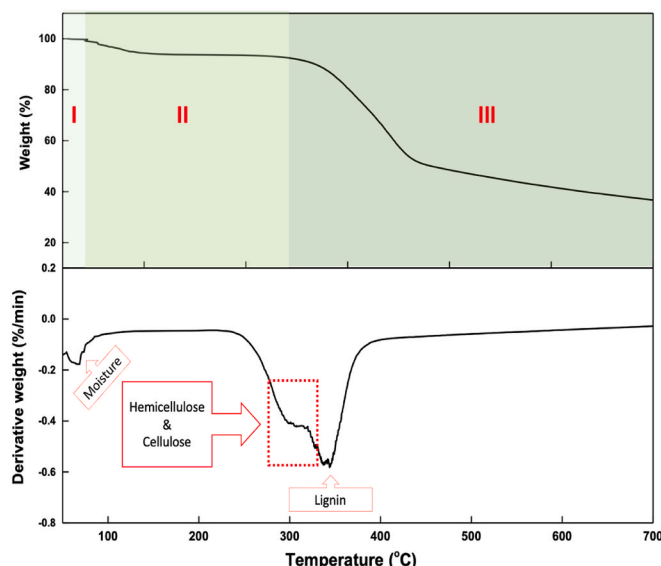


Fig. 2. Thermogravimetric Analysis (TGA) of rice husk.

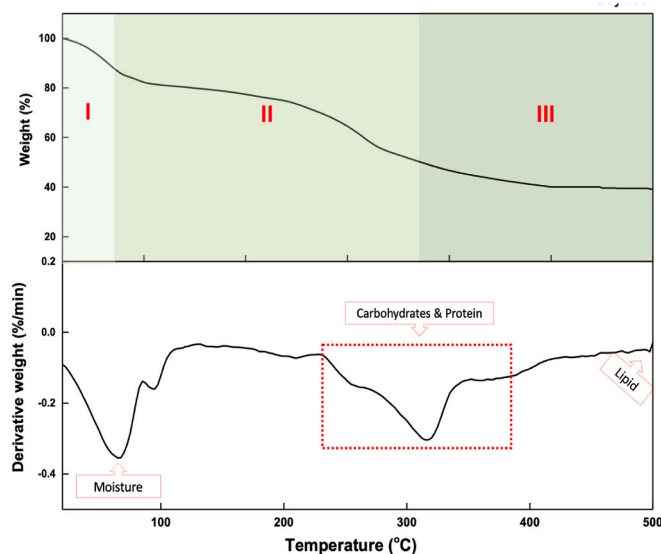


Fig. 3. Thermogravimetric Analysis (TGA) of soybean.

support to plants and exhibits higher thermal stability compared to cellulose and hemicellulose. The decomposition of these components during TGA leads to the generation of additional volatile gases and the formation of solid residues. The residue remaining at the end of this phase corresponds to solid carbonaceous material, which may consist of char and ash. This residue can be further explored for its potential applications, such as biochar production or as a precursor for the synthesis of value-added materials in agriculture [48].

TGA analysis of rice husks provides valuable information about their thermal decomposition behaviour and the presence of various organic and volatile components. This knowledge can be utilised for the efficient utilisation of rice husk biomass in various applications. For example, volatile gases released during thermal decomposition can be captured and utilised as a source of energy, such as in biofuel production or heat generation [49]. The rich organic content and thermal stability of rice husks make them a promising and renewable resource for sustainable development and transition to a more environmentally friendly and resource-efficient future.

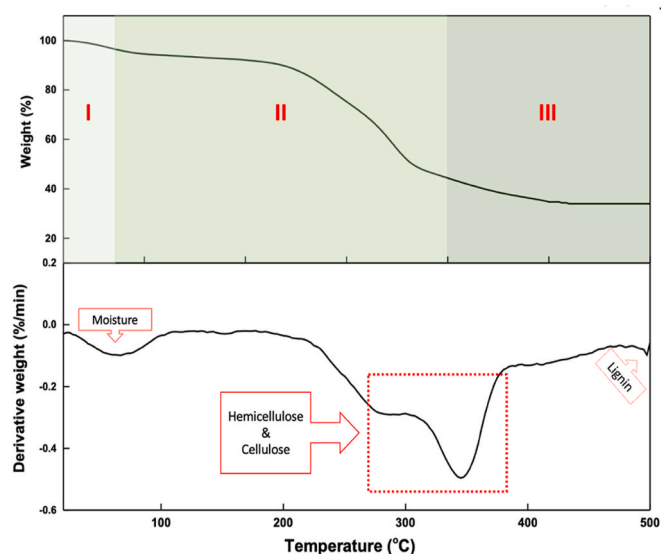


Fig. 4. Thermogravimetric Analysis (TGA) of lemon myrtle.

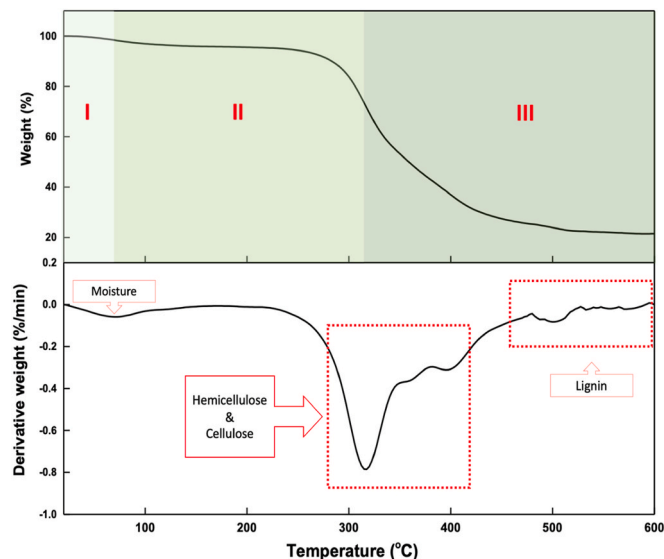


Fig. 5. Thermogravimetric Analysis (TGA) of waste coffee ground.

### 3.3.2. Soybean

Soybean (*Glycine max* (L.) Merr.) is a versatile legume widely cultivated in eastern Asia and is used for various purposes, including food production and animal feed [50]. It has also gained significant attention as a potential feedstock for bio-oil production because of its complex composition, as it has good stability in its oxidation degree to study as an alternative for biodiesel usage [51]. It contains approximately 50 % protein, lipid, and carbohydrate components, and 18 %–24 % oils, making it a complex and heterogeneous material [52]. The complex and heterogeneous nature of soybeans makes them interesting materials for thermal analysis.

In the first phase, an initial weight loss of 15.71 % was observed at approximately 48 °C (Fig. 3). This initial weight loss is often attributed to the evaporation of the surface moisture and volatile compounds present in the soybean sample. The volatile components, such as water and low-molecular-weight organic compounds, evaporated and contributed to the observed weight loss. The second phase started at approximately 60 °C, where a gradual weight loss of 13.27 % occurred. The most significant weight loss in this phase was observed at 3310 °C

with a mass reduction of 18.22 %. This weight loss is primarily attributed to the decomposition and combustion of the organic compounds present in soybeans, particularly proteins and carbohydrates. As the temperature continues to rise, these organic compounds undergo thermal degradation and combustion, leading to the release of volatile gases and the formation of solid residues. The dip observed in the TGA curve at 310 °C denotes substantial transformation of the organic components and their subsequent release as gases.

Above 320 °C, the TGA curve entered the third phase, which was concluded at 480 °C. In this phase, further weight loss of 12.81 % occurred, leaving approximately 40.16 % of the initial mass. This weight loss is mainly associated with the disintegration and decomposition of the lipid content in soybeans. Lipids, which have higher thermal stability than proteins and carbohydrates, undergo thermal breakdown and release gases during this phase. The endothermic nature of the decomposition process indicates that energy absorption is required for the breakdown of lipid components [53].

### 3.3.3. Lemon myrtle

Lemon myrtle (*Backhousia citriodora*) is an aromatic plant native to Australia and is known for its strong lemon-like scent and flavour, which are used in various applications, including food, fragrance, and bio-oil production [54]. In the first phase of the TGA, a weight loss of 6.30 % was observed at 60 °C. This initial weight loss is typically attributed to the evaporation of surface moisture and volatile compounds present in the lemon myrtle samples. These volatile components, including water, vaporise at relatively low temperatures and contribute to the observed weight loss shown in Fig. 4.

The second phase started at approximately 70 °C and extended up to 345 °C, with a steady total weight loss of 17.38 %. The most prominent dip in the TGA curve occurred at 345 °C, where the weight loss reached a peak of 31.84 %. This phase is indicative of the decomposition of the main organic constituents present in lemon myrtle, such as essential oils, terpenes, and other volatile compounds, in which thermal degradation and combustion occur, leading to the release of volatile gases and the formation of solid residue [55].

In the third phase, there is a further weight loss of 10 %, which is usually lignin, and the residue remaining at the end of this phase corresponds to only 34.81 % of the initial mass [56]. This weight loss also suggests the decomposition of more complex and thermally stable components present in lemon myrtle, such as polyphenols, flavonoids, and other organic compounds [55]. The decomposition of these compounds leads to the generation of additional volatile gases and the formation of char or ash. Therefore, it has been proven to have high volatile matter and low ash content, making it suitable for bio-oil production and feasible for co-pyrolysis with other materials.

### 3.3.4. Waste coffee ground

Waste coffee grounds, a by-product of coffee brewing, have gained attention as a potential renewable resource because of their high carbon and low ash contents which are suitable for thermal conversion processes such as combustion [57]. Andrade et al. used TGA to analyse the mass loss of WCG during heating and to determine the acid-base behaviour of biochar obtained from the carbonisation of waste coffee grounds for energy storage purposes, whereas Kerolli Mustafa et al. [58] determined the feasibility of using waste coffee grounds as thermal insulation or catalyst support. This demonstrates the wide usage of waste coffee grounds and their potential for energy production and other applications.

In the first phase of the TGA shown in Fig. 5, a weight loss of 4.15 % was observed at 70 °C. This initial weight loss is typically attributed to the evaporation of surface moisture and volatile compounds present in waste coffee grounds. In the second phase, a significant dip occurred in the TGA curve at 3320 °C where the weight loss peaked at 40.18 %. This phase represents decomposition which includes both endothermic and exothermic thermal occurrences of the main organic constituents

present in spent coffee grounds, such as hemicellulose and cellulose, and other complex organic compounds such as proteins [59]. The onset temperature of this phase at 284.10 °C indicates the initiation of thermal degradation and combustion of these organic components. The release of volatile gases and the formation of solid residues contributed to the observed weight loss. The high weight loss in this phase suggests the presence of substantial organic content in the spent coffee grounds, which can be utilised for energy production through processes such as pyrolysis or combustion.

In the third phase, there was a gradual weight loss of 11.72 % and 19.89 %, respectively, indicating the decomposition of more complex and thermally stable components (lignin) in the spent coffee grounds. The residue remaining at the end of this phase corresponded to only 24.32 % of the initial mass, highlighting the significant decomposition and volatilisation of the organic components. Nonetheless, the significant weight loss observed during the decomposition stages suggests the presence of organic compounds that can be utilised for energy recovery or converted into value-added products such as biochar or biofuels [60].

### 3.3.5. Empty fruit bunch

Empty fruit bunch (EFB) refers to residual fibre, which is mostly lignocellulosic and remains after the extraction of palm oil from oil palm fruits [61]. In the first phase, an initial weight loss of 6.02 % was observed at 60 °C shown in Fig. 6. This weight loss is typically attributed to the evaporation of surface moisture and volatile compounds present in the EFB samples which is consistent with other organic materials, as evaporation occurs at relatively low temperatures [62].

The second phase starts at an onset temperature of 329.07 °C with two noticeable dips in the weight derivative curve. The first dip occurred at a lower temperature, resulting in a weight loss of 27.45 %. This dip can be associated with the decomposition of hemicellulose, which is one of the main constituents of EFB. The subsequent dip, which is the largest dip in the curve, occurs at 350 °C with a weight loss of 43.29 %, signifying the decomposition and combustion of the remaining organic components, such as hemicellulose, cellulose, and other complex organic compounds [63]. In the third phase, further weight loss is observed, with 23.62 % of the residue remaining at 360 °C. This weight loss implies the decomposition of more complex and thermally stable components present in EFB, such as higher molecular weight lignin and other organic compounds. The residue remaining at the end of this phase corresponds to solid carbonaceous material, which may consist of char and ash.

The weight loss observed in different phases indicates the presence of various organic and volatile components in EFB, which can be further explored for energy production through processes such as pyrolysis, gasification, or combustion. In addition, the solid residue remaining after thermal decomposition can be investigated for its potential application in biochar production or as a precursor for biocomposite materials [64]. Nonetheless, the thermal performance of EFBs makes them a promising feedstock for various thermal conversion processes, contributing to the sustainable utilisation of this abundant agricultural residue.

### 3.3.6. High-density polyethylene

High-density polyethylene (HDPE) is a thermally stable polymer known for its resistance to thermal degradation and high melting point. When subjected to TGA, HDPE displays distinct phases that reveal its thermal behaviour. In the first phase, a slight weight loss of 0.8 % was observed at 180 °C. This initial weight loss can be attributed to the evaporation of volatile compounds such as residual solvents or moisture, which may be present on the surface of the HDPE sample. This insignificant weight loss indicates the thermal stability of HDPE. The polymer chains remained intact, and no noticeable degradation or decomposition was observed, even at high heating rates (40 °C/min), as reported by Kumar et al. in the same temperature range as in the TGA analysis [65].

The second phase is a relatively flat weight curve which confirms HDPE's resistance of HDPE to decomposition and thermal degradation

within the tested temperature range, as no significant changes in weight were observed, which was also aligned with the study done by Al-Bayaty et al. [66]. However, TGA is still a widely used thermal analytical technique applied to polymers, including HDPE plastics, to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties.

The third phase of TGA revealed that a substantial portion of the initial mass remained as residue at 4480 °C With 92.08 % of the mass remaining intact, HDPE demonstrated remarkable thermal stability even at elevated temperatures. Briceno et al. [67] analysed the thermal degradation of HDPE and polypropylene (PP) mixtures and found that the degradation process can be described as a single-step degradation process, influenced by the proportion of the two plastics. The HDPE/PP mixtures with higher PP ratios tended to lower the onset temperature of the degradation of the mixture. This highlights HDPE's ability of HDPE to withstand high decomposition temperatures, prevent significant weight loss, and maintain its structural integrity and properties, making it a desirable material for numerous applications. Its resistance to decomposition and ability to withstand high temperatures make it suitable for applications in the packaging, automotive, and construction industries. Additionally, the high residue percentage observed at temperatures above 480 °C suggests the potential for HDPE recycling and its use in energy recovery processes, such as incineration or pyrolysis.

## 3.4. Pyrolysis

The yields of the different types of organic waste and HDPE in terms of the conversion of char, oil, gas, and feedstock are shown in Fig. 7. The compositions of the different organic wastes were apportioned into three by-products based on the yields obtained via pyrolysis. EFB and SB produced the highest oil at 26.49 % and 25.25 %, respectively, in agreement with other researchers' findings [68].

The higher gas yield may be due to inefficient condensers or gas compressors during the pyrolysis process which causes a failure to convert to oil. The results suggest that the feedstock composition has a significant impact on the yield of different products. For instance, SB (71.99 %) and WCG (74.89 %) had a higher char yield than other feedstocks, which could make them more suitable for applications that require a solid residue, such as soil amendment or carbon sequestration, similar to Xiong et al. [69]. In contrast, EFB (27.79 %) and LM (31.07 %) showed higher gas yields, making them more suitable for energy applications. However, HDPE produced the least amount of oil (2.67 % and

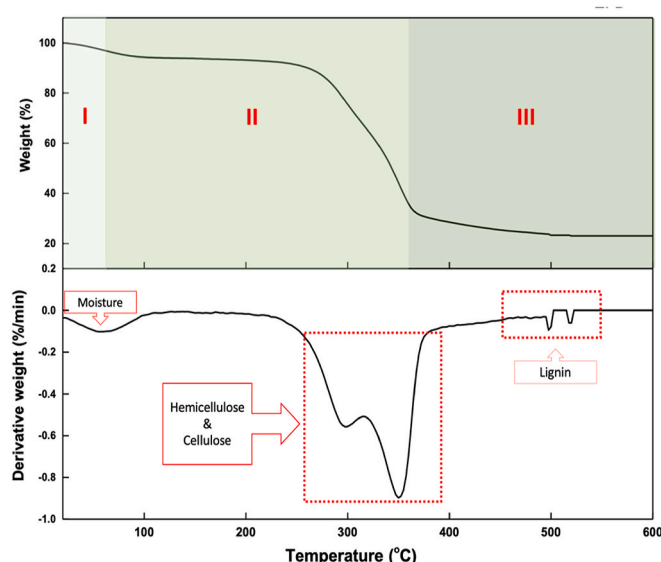


Fig. 6. Thermogravimetric Analysis (TGA) of empty fruit bunch.

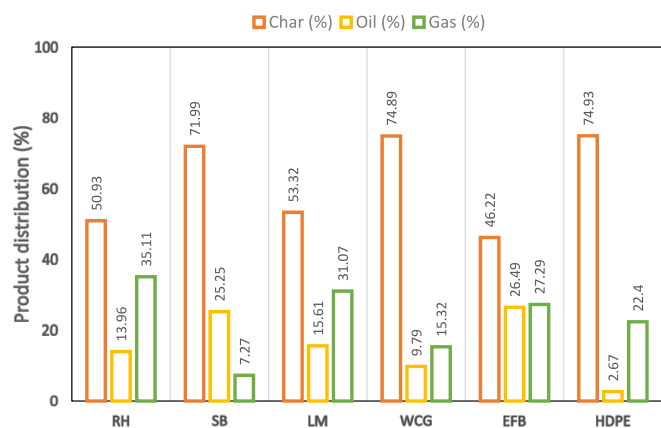


Fig. 7. Yield distribution of pyrolysis of organic waste and HDPE.

22.4 % of gas). This also implies that there is still an opportunity to condense excess gas into a useable liquid product.

#### 4. Predictive mathematical modelling

In the realm of thermal conversion technologies, incineration or pyrolysis stands as a preeminent and practical avenue for harnessing energy from both biomass and polymer waste to ensure the efficacy of the incineration process; thus, a comprehensive understanding of the composition and attributes of waste is imperative [70]. While attributes such as proximate and ultimate analysis outcomes are vital as preliminary assessments for both high and low heating values (HHV and LHV), they can be a paramount parameter to be implemented as predictive modelling for the eventual selection of feedstock in energy recovery studies [71].

The presented Table 4 outlines the calorific heating values of distinct feedstocks derived from the ultimate analysis, substantiating a direct connection between the previous preliminary analyses and the predictive value they hold for the eventual heating values (HV). This linkage emphasises the practicality of these initial assessments in anticipating the heat energy content of different feedstock materials. The Dulong formula, known as the Dulong-Petit law, establishes a relationship between the Higher Heating Value (HHV) of fuel and its elemental composition, focusing specifically on the weight fractions of carbon, hydrogen, and sulphur [72]. By contrast, the Modified Dulong formula expands its considerations to encompass oxygen and nitrogen within the composition of the fuel. These formulas yield specific energy content percentages, such as Dulong (18.70 %–40.98 %), Modified Dulong (33.63 %–67.75 %), Vandralek (11.93 %–44.50 %), and Lower Calorific Value (8.31 %–29.35 %). The outcomes revealed discrepancies in the energy content estimations, emphasising the significance of the chosen calculation approach in evaluating the energy potential across these feedstock varieties.

An alternative estimation technique, the Vandralek formula, parallels the Dulong method for predicting both the HHV and Lower Heating Value (LHV) of fuels. However, it distinguishes itself by considering the oxygen content of each feedstock. It is imperative to highlight that the LCV computation, as part of these formulaic methods, assumes the premise of complete combustion. However, this calculation neglected

Table 4  
HCV and LCV estimates through mathematical prediction.

Types	RH	SB	LM	WCG	EFB	HDPE
Dulong	18.70	16.58	21.43	23.94	21.67	40.98
Mod. Dulong	50.58	67.75	52.80	57.21	54.54	33.63
Vandralek	14.64	11.93	18.33	21.72	18.60	44.50
LCV	14.49	8.31	16.67	17.47	16.51	29.35

any potential energy loss arising from incomplete combustion or other contributing factors. Consequently, the outcome of the LCV estimation using these formulas might not fully encapsulate the intricate realities of combustion processes.

The primary distinction between Higher Calorific Value (HCV) and Lower Calorific Value (LCV) lies in the treatment of the reaction by-products. In the case of HCV, the reaction by-products are permitted to cool to room temperature, allowing a portion of the heat to be recovered. Conversely, in the LCV (Table 4), these by-products are allowed to escape, leading to the loss of a quantifiable amount of heat carried away by steam and a noteworthy dissimilarity in how heat is managed. Furthermore, the LCV was calculated as the difference between the heat carried away by steam and HCV. This method ensures that the LCV represents a net measure that accounts for the heat lost through the steam in the process. Therefore, the fundamental contrast between HCV and LCV stems from the approach used to manage combustion by-products and their associated heat losses [73]. HCV encapsulates the total heat release without considering the heat carried away by steam, whereas LCV gauges the net heat liberated, accounting for steam-induced heat losses.

##### 4.1. Relative error

A comparison of the relative error (%) values derived from the different calculation formulas applied to various feedstock types is presented in Table 5. Notably, the experimental values were obtained from other studies that solely tested similar types of feedstocks individually for their calorific values. Relative errors were calculated and compared, showing that the Dulong formula varied, with RH, SB, and WCG displaying underestimations ranging between  $-10\%$  to  $-35\%$ , whereas LM, EFB, and HDPE exhibited slight overestimations of  $1\%$ – $25\%$ . The Modified Dulong formula accentuates the major underestimations observed for all feedstocks as high as  $-451\%$  for SB, except for HDPE of  $18\%$ . The Vandralek formula introduces further distinctions, resulting in a positive error in close range but an underestimation for HDPE ( $-8\%$ ). This succinct analysis underscores the formulas' diverse performance across feedstock types, revealing both strengths and limitations in accuracy.

The obtained results fell within acceptable bounds, consistent with the findings of other researchers who employed a similar methodology to derive the HHV values via ultimate and proximate analyses [74]. Their results fall within the  $15.35\%$  range, which closely mirrors the relative errors presented in the table. This consistency reinforces the reliability and validity of the results, thereby bolstering the credibility of the applied approach. Nzihou et al. [75] have also established that Dulong and Vandralek yield small relative errors, thus serving as efficient tools for efficient estimation of HCV values from ultimate analyses as the advantage stems from the precision of elemental values. This implication extends the formulas' potential as rapid mathematical models to pre-assess feedstocks and streamline selection for subsequent studies related to biofuels, energy, or combustion.

##### 4.2. Correlation with preliminary analyses and pyrolysis

The calorific potential of the feedstock is intricately tied to its water

Table 5  
Comparison of relative error (%) for different formulas across various feedstocks.

Types	Experimental (Sources)	Dulong	Mod. Dulong	Vandralek
RH	16.51 [76]	-13	-206	11
SB	12.30 [77]	-35	-451	3
LM	19.48 [78]	-10	-171	6
WCG	24.08 [60]	1	-138	10
EFB	28.99 [79]	25	-88	36
HDPE	41.20 [80]	1	18	-8



content, creating a direct correlation through further scrutiny using proximate analysis and TGA, as shown in Fig. 8. When set into perspective, a pattern was clearly revealed: as the moisture content decreased, the corresponding temperature tended to increase. Parikh et al. substantiated this assertion using a comprehensive model encompassing 550 datasets, yielding a significant error margin of 3.74 %. This signifies that fuels with an elevated moisture content tend to possess a lower HHV, leading to reduced net energy generation upon combustion [81]. Jiang et al. also validated that lower moisture content and less energy are spent on evaporation, enabling the temperature to increase more rapidly [82]. Consequently, feedstocks with a lower water content are preferable for energy generation.

The VM content is directly correlated with fuel reactivity, influencing both the speed of fuel-to-gas transformation and ignition ease. This correlation contributes to enhanced fuel conversion rates because the presence of abundant oxygen and volatile matter signifies the potential for generating substantial vapour quantities during the conversion processes [83]. However, Vega et al. [84] asserted that low fixed carbon and high volatile matter contents are favourable as they promote rapid burning, which is beneficial for fuel efficiency. Ultimately, predictive modelling, as shown in the preceding sections, establishes a correlation between the initial analyses and eventual heating values. This relationship guides the selection of suitable feedstock for bio-oil production.

As Jahirul et al. [85] reiterated, a significant VM content fosters devolatilisation reactions, particularly prominent in pyrolysis processes, yielding permanent gases, condensable vapours (bio-oil), and char. Additionally, researchers have claimed that a high fixed carbon content is indicative of a high HHV [82]. This is substantiated by the proximate analysis results in Fig. 9 which show an inverse correlation between the fixed carbon and volatile matter. This relationship is inherent to combustion and thermal decomposition. The increased fixed carbon signifies a stable, carbon-rich material, yielding controlled energy release, as shown in Fig. 10, when comparing the fixed carbon obtained from proximate analysis and the actual char yield obtained from the feedstock after pyrolysis. In contrast, a higher volatile matter content implies vaporising elements, accelerating ignition, and releasing energy. The fixed carbon content from the proximate analysis was positively correlated with the amount of char produced during pyrolysis. This is attributed to the role of fixed carbon as a component within the biomass or coal that remains after the volatile matter is expelled. It was subsequently transformed into char during pyrolysis. As evidenced by Sun et al. [86], pyrolysing at approximately 500 °C able to recover char of 48.02 % for fixed carbon spanning 14.36%–85.57 % for various biomass feedstocks. Biomass with a higher fixed carbon content, approximately 80 % in cases of robust outer shells, tends to generate greater char. Focusing on the biomass feedstock in Fig. 10, the correlations highlight

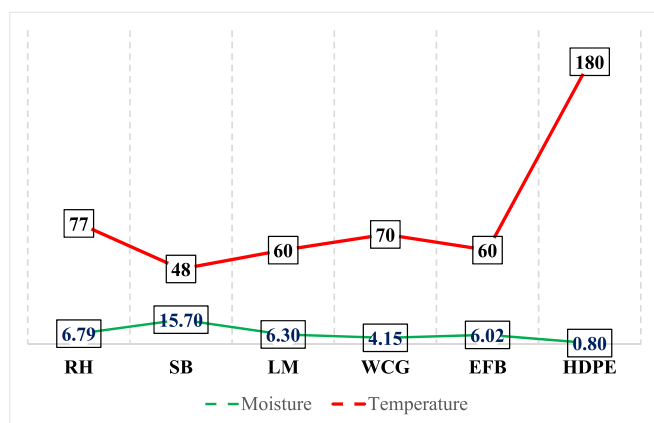


Fig. 8. Moisture content loss for feedstocks.

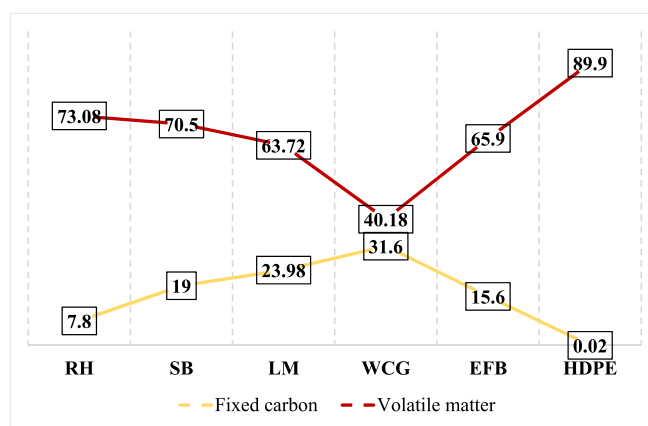


Fig. 9. Relationship between volatile matter and fixed carbon for feedstocks.

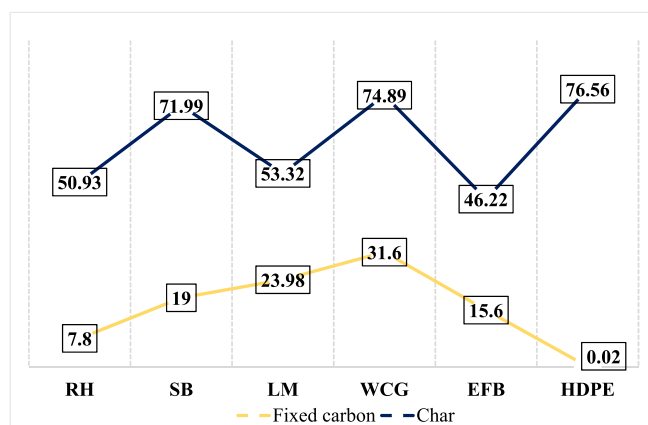


Fig. 10. Relationship between fixed carbon and char for feedstocks.

the role of cellulose and lignin in promoting fixed carbon production in biochar. Higher fixed carbon generation was observed in feedstocks with elevated lignin content compared to that of cellulose. This distinction can be influenced by the greater thermal stability of lignin during pyrolysis, contributing to increased fixed carbon production in biochar as the lignin/cellulose content in biomass rises, as shown in the TGA of RH and EFB.

The volumes of oil and gas generated during pyrolysis exhibit a positive correlation with the volatile matter content of the feedstock. Volatile matter has a direct and relative correlation with the quantity of gas and oil produced during thermal conversion processes, particularly pyrolysis. However, the oil production volume is significantly influenced by the efficiency of the condenser in converting vapour into oil.

In a different context, Bayartsaikhan et al. [87] revealed that the volatile content of brown coal is dependent on temperature and reaction duration, with less than 2 % volatile content in their estimations. Conversely, thermal pyrolysis of HDPE indicates that higher volatilisation temperatures promote the cracking of volatiles, leading to reduced carbon chain length and subsequently decreased oil yield, as claimed by Chen et al. [88]. This was confirmed by the lower conversion rate depicted in Fig. 11, indicating a suboptimal temperature for efficient product conversion. Thus, the optimal temperature depends significantly on the material type. Initial insights from Thermogravimetric Analysis (TGA) can serve as a guide, providing accurate data for pinpointing the optimal volatile matter-to-gas conversion temperature.

## 5. Conclusion

The conclusion underscores the robust performance of the Dulong

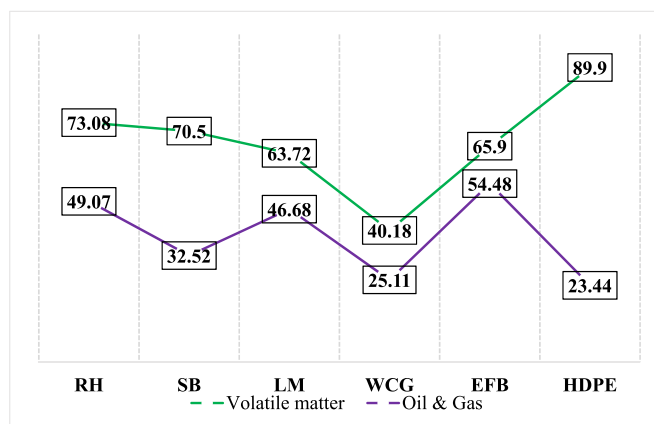


Fig. 11. Relationship between volatile matter and product for feedstocks.

and Vandralk formulas, revealing minimal relative errors of 1 % and 3 % respectively in mathematical modelling based on ultimate and proximate analyses while modified Dulong shows a wide range of relative error (18 % to –206 %). This high level of accuracy by Dulong and Vandralk, validated by congruent findings from preliminary analyses and subsequent pyrolysis results, establishes a firm correlation, affirming the reliability of these formulas in estimating calorific content and energy storage potential. Their efficiency in providing swift estimations not only streamlines the assessment process but also conserves valuable time and resources. While alternative formulas exist, their effectiveness may be hindered by the requirement for intricate knowledge of parameters (temperature, pressure, blending ratio, feedstock sizing, etc.), particularly those that may not be well-defined within the context of waste materials. Expanding upon these findings, it becomes evident that the utilisation of the Dulong and Vandralk formulas holds significant implications for future research endeavours and practical applications in waste management and energy production. By accurately gauging the calorific content and intrinsic energy storage of prominent biomass and polymer waste sources, these formulas offer a pathway towards optimised resource utilisation and sustainable energy generation. Furthermore, their streamlined application facilitates informed decision-making processes, guiding policy interventions and technological innovations aimed at mitigating environmental impacts and advancing circular economy initiatives.

However, it's important to acknowledge potential limitations associated with the use of these formulas, such as variations in feedstock composition and combustion conditions, which may impact accuracy. Future research efforts should aim to address these challenges through refinements in formula application and the development of comprehensive models that account for diverse waste streams and environmental variables. In conclusion, the alignment of empirical data and theoretical models reinforces the reliability of Dulong and Vandralk formulas in precisely determining calorific values. These formulas play a crucial role in driving progress in waste-to-energy practices and fostering sustainability in waste management practices, making them indispensable tools for a more sustainable and resource-efficient future as it ensures accurate estimation.

#### CRedit authorship contribution statement

**Chiun Chao Seah:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization, Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Saiful Hafiz Habib:** Writing – review & editing, Validation. **R. S.R.M. Hafriz:** Writing – review & editing, Validation. **A.H.**

**Shamsuddin:** Validation, Supervision, Resources, Project administration. **N.M. Razali:** Supervision, Resources, Project administration. **A. Salmiaton:** Validation, Supervision, Resources.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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