Simulation And Analysis Of Calorific Value For Biomass Solid Waste As A Potential Solid Fuel Source For Power Generation

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Biomass solid waste (BSW) generation in Malaysia is rapidly increasing as a result of nation's industrialization, urbanization, and population growth. Thermochemical conversion of BSW to produce energy is not straightforward due to fuel's high moisture content, low heating value, and poor grindability. Accessing different combinatorial scheme of BSW may help to mitigate above-mentioned issues while maintaining attractively high energy outputs. In this work, calorific values and ultimate analyses of a wide variety of BSW reported in literature were compiled. Based on the collected data, two empirical correlations to predict high heating value (HHV) of BSW were developed using a multiple regression method. The developed correlations were (i) $HHV = 908.37C + 2942.94H + 4439.73S + 518.92O - 63558.52 (\text{municipal solid waste})$ and (ii) $HHV = 382.62C - 368.16H + 2788.24S - 37.83O + 926.26 (\text{biomass/biochar})$ where, C, H, O, N, and S represent biomass content in a form of elemental carbon, hydrogen, oxygen, nitrogen, and sulfur, respectively. The accuracies of the correlations were verified by comparing the predicted values with those experimentally determined. Thermogravimetric analysis was used to analyze BSW combustion behavior and retrieve important combustion parameters. The best-fit correlations obtained in this work had R_2 values of 0.98 (MAPE of 3.2%) and 0.92 (MAPE of 7.1%) for municipal solid waste and biomass/biochar samples, respectively. Moreover, the correlations were fairly accurate in predicting HHV of different BSW combination with prediction error of less than 15%. The correlations developed in this work could be instrumental for a precise determination of different combination of solid biomass.

Keywords: Biomass solid waste, calorific values, bomb calorimeter, power generation

1. Introduction

Rapid increase in greenhouse gas emissions (e.g., CO_2) from combustion of non-renewable fossil fuels and future demands for sustainable energies have encouraged researchers and policy makers to look for renewable energy sources and develop advanced energy conversion technologies. Shifting to renewable energies help to ensure energy availability, diversify energy portfolios, and abate climate change issues. Promoting renewable energies results in green development. At the same time, it provides numerous benefits to communities such as increased food production, reduced environmental risks, and improved social, financial, and economic well-being [1]. Malaysia has

pledged to use biomass as a fuel source in thermal power plant in order to achieve 50% green energy in the energy mix by 2050.

Biomass solid waste (BSW) is gaining popularity as a renewable resource due to its abundance in nature, rapid renewability, net below zero CO_2 emission, and low cost [2, 3]. Among the potential biomass conversion technologies (emerging and mature) to be considered to process BSW resource include combustion, gasification, pyrolysis, alcoholic fermentation, supercritical fluid processing, anaerobic digestion, and photosynthetic microbial fuel cells [4]. Biomass has a potential to be used as a fuel source in power plants to generate energy through combustion process. Biomass is considered as a "carbon-neutral" resource because it sequesters CO_2 during its growth, which compensates for the CO_2 released when combusted [3]. Pollution in the form of acid rain and other pollutants can be reduced because biomass emits less sulfur dioxide and nitrogen oxide to the atmosphere.

Despite inexpensive and abundant, BSW however has its limitations as a direct feedstock for energy production. BSW possesses high moisture content, low bulk density, poor heating value, and biodegradability; likely will result in poor combustion efficiencies and low energy outputs [5]. During combustion process, elemental chlorines present in the BSW can form corrosive hydrogen chloride that can damage boiler unit in thermal power plants [6]. Utilizing a single type of biomass for energy production is desirable as it provides a relatively stable energy output without a significant variation in the composition of the flue gas to be treated downstream. However, obtaining a single type of BSW source might be challenging from sourcing and sorting point of view. Researchers might be able to go around the above-mentioned challenges by combining two or more type of biomass in their fuel mix. Mixed-biomass approach allow for a higher degree of freedom in the selection of biomass as solid fuels.

One important metric to consider when evaluating potential of biomass as fuel source for energy production is biomass calorific values. Calorific value of a solid fuel can be expressed as a low heating value (LHV) or a high heating value (HHV). LHV refers to the amount of heat released by a fuel source during combustion process with water in its gaseous state as a product while HHV is based on water in its liquid state [7, 8]. Calorific values of BSW can be measured experimentally with a bomb calorimeter or mathematically predicted based on physicochemical properties of the materials [7–9]. It is worth to mention that a precise determination of calorific values of biomass through experimental approaches is complicated, time-consuming, and

labor intensive. There are many proposed models to predict heating values of solid fuels based on the fuels' chemical analysis, proximate analysis, and ultimate analysis. Among the popular model is Dulong's model which is originally developed to predict the heating value for coal samples. Tillman back in 1978 developed two new equations to estimate calorific values of biomass from its final analysis and found that the biomass calorific values strongly depend on the biomass carbon contents [9]. Models to predict calorific values of a wide range of biomass have been proposed by Yin [9], Huang et al. [10], and Callejón-Ferre et al. [11].

We should highlight here that prior works mostly focus on calorific value evaluation of a particular type of biomass. Therefore, the developed correlations might be accurate to a narrow range of biomass samples only. The correlations accuracies might be uncertain when considering different class of solid fuels, for example, municipal solid waste (MSW) or different combinations of biomass. In addition, there is still lack of studies on combustion performances and precise determination of calorific values for different combinations of BSW. Large-scale energy production utilizing only one type of BSW requires unnecessary steps (i.e., materials sorting). Therefore, coming up with a model to precisely predict calorific values of different mix of BSW is instrumental in this area. Since experimental determination of calorific value are tedious work, one may opt for mathematical approach. Mathematical models can be produced with ease at a faster rate and lower cost [7, 8]. Hence, this approach has been adopted by Akkaya and coworkers [12, 13] for a precise determination of calorific values of different coal samples.

Herein, we report two models to predict calorific values of different BSW and their combinations using a mathematical approach. The accuracies of the predictive models are then compared to established models (i.e., Dulong and Steur). For validation, the calorific values predicted by the models were compared with those experimentally determined using bomb calorimeter. Thermogravimetric analysis was used to monitor the fuel's burning profile and retrieve combustion parameters [14]. Coats Redfern method was selected to evaluate BSW combustion kinetics and combustion reactivities.

2. Experimental

2.1. Development of calorific value models based on ultimate analysis

Development of empirical correlations to predict calorific values of different BSW samples involves an extensive literature survey and data collection from previously reported works [15–22]. Ultimate analyses and calorific values of

32 different samples were compiled and analyzed in the Microsoft Excel: (1) MSW – wood, tires, paper, rubber, yard waste, textile, etc. (2) biomass – sawdust, coconut fiber, palm kernel shell, etc. (3) biochar – rice husk, corn straw, wine pine, oil palm trunk, etc. Two new correlations were developed using linear regression approach. Percentage error (Eq. (1)) values were used as indicators to measure deviation between the predicted and experimental calorific values. In Equation 3 below, CV_{pred} is predicted calorific value ($kJ.kg^{-1}$) and CV_{meas} is measured calorific value ($kJ.kg^{-1}$).

$$\text{Percentage error} = \frac{CV_{pred} - CV_{meas}}{CV_{meas}} \times 100\% \quad (1)$$

The developed correlations were then compared with established correlations (i.e., Dulong and Steur) to determine which correlations are more precise in predicting biomass heating values. If prediction error is close to zero, the correlation is indicated as the best regression line [23, 24]. To select a statistically suitable calorific value correlation for BSW samples, mean absolute percentage error (MAPE) values are used as indicators (Eq. (2)). MAPE is a simple measure of how close the predicted calorific value is to experimental data, with lower MAPE values imply better correlation accuracy. In the equation below, HHVpred and HHVexp are predicted and experimental high heating value in kJ/kg.

$$\text{MAPE} = \frac{1}{n} \sum_{n=1}^{n} \left(\frac{HHV_{pred} - HHV_{exp}}{HHV_{exp}} \right) \times 100 \quad (2)$$

2.2. Experimental evaluation of biomass calorific values and burning profiles

Calorific values of BSW samples were experimentally determined using an oxygen bomb calorimeter (PARR-1314) performed in accordance with the ASTM D5865-13 standard. The tests were conducted in an air environment and lasted for approximately 10 min at 35 psi ($\sim$2.38 atm). Measurements were repeated for each sample and average results were recorded. For bomb calorimeter tests, 1.0 grams of samples (measured using analytical balance) were used. Five locally procured BSW samples were shredded into a smaller size prior to testing. To experimentally determine calorific values of BSW mix, five combinations of solid samples with 1:1 ratio by weight were used.

Three BSW combinations were randomly selected to for thermogravimetric analysis (TGA). The samples chosen were multiple plastic/biochar, used tires/biochar, and used tires/textiles. Thermal analyses of different combination of BSW samples were performed using a Mettler Toledo

TGA/DSA 3+. A solid sample was filled in a crucible and heated under a continuous flow of air (100 ml.min^{-1}) from room temperature to 900 °C with a ramp rate of 20 °C.min^{-1}. Sample weight loss (TG curve) and differential weight loss (DTG curve) as a function of time or temperature were recorded.

2.3. Quantification of biomass solid waste combustion parameters

BSW combustion performances can be assessed from the TGA curve. Key combustion characteristics such as ignition temperature, burnout temperature, and combustion index can be calculated from the TGA profiles. Ignition temperature, (T_i) is determined by locating the temperature at which the sample began to burn. Meanwhile, burnout temperature, (T_b) is a temperature at which the burning rate reached 1%.min^{-1} at the end of DTG curve. Alternatively, T_b can also be taken at temperature where conversion reaches 99% [25]. Both T_b and Ti have a similar unit of degree Celsius (°C). Combustion index (S) is calculated from Eqs. (3) and (4) where DTG_{max} is the maximum combustion rate, DTG_{mean} is the average conversion rate between T_i and T_b, β is the heating rate, α_{Tb} are fractions of material degraded at T_b, and α_{Ti} are fractions of material degraded at T_i [26, 27]:

$$S = \frac{DTG_{max} \times DTG_{mean}}{T_i^2 \times T_b} \quad (3)$$

$$\frac{dm}{dt} \text{ mean} = \frac{\alpha_{Tb} - \alpha_{Ti}}{(T_b - T_i)/\beta} \quad (4)$$

Based on these key parameters, a few comments can be made. A solid fuel with high T_i usually indicates a fuel source with a high thermal stability. A high T_b value indicates a fuel that is difficult to burn, necessitating a longer retention time and high heat flow for a full conversion. Lastly, high combustion index values indicate good combustion performances.

2.4. Evaluation of biomass solid waste combustion kinetics

To model mass loss with the Arrhenius's law, the conversion degree (α) is represented by Eq. (5). Rate of heterogeneous solid-state reactions on the other hand is calculated from Eq. (6).

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (5)$$

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k(T) f(\alpha) = \frac{C}{\beta} \exp\left(-\frac{E_A}{RT} f(\alpha)\right) \quad (6)$$

where $\beta = \frac{dT}{dt}$.

For Eq. (5), m_o, m_t, and m_f are initial mass of sample (g), mass of sample at time t (g), and final mass of sample (g), respectively. Meanwhile for Eq. (6), symbols/variables k, T, R, C, E_A and α are temperature dependent reaction constant (s^{-1}), absolute temperature (K), universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), pre-exponential factor (min^{-1}), activation energy ($kJ \cdot mol^{-1}$), and conversion degree, respectively.

Combustion kinetic parameters are calculated using the Coats Redfern method. The Coats Redfern model is a model-free method used to calculate activation energy (E_A) and pre-exponential parameters by varying the reaction order (n). Simplified Coats Redfern model are shown in Eqs. (7) and (8). Linearized form of Coats Redferns model was obtained through simple mathematical manipulation (Eqs. (9) and (10)).

$$\ln \frac{\left(1 - (1 - \alpha)^{1-n}\right)}{T^2 (1-n)} = \ln \frac{CR}{\sigma E_A} - \frac{E_A}{RT} \left(\text{ for } n \neq 1 \right) \quad (7)$$

$$\ln \frac{(1 - (1 - \alpha))}{T^2} = \ln \frac{CR}{\sigma E_A} - \frac{E_A}{RT^2} \left(\text{ for } n = 1 \right) \quad (8)$$

$$y - \text{ axis } = \ln \frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n)}, x - \text{ axis } = \frac{1}{T} \left(\text{ for } n \neq 1 \right) \quad (9)$$

$$y - \text{ axis } = \ln \frac{1 - (1 - \alpha)}{T^2}, x - \text{ axis } = \frac{1}{T} \left(\text{ for } n = 1 \right) \quad (10)$$

where n, T, σ, R, C, and EA are reaction order, absolute temperature (K), heating rate ($K \cdot min^{-1}$), universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), pre-exponential factor (min^{-1}), and activation energy ($kJ \cdot mol^{-1}$), respectively. Alpha (α) on the other hand is conversion degree (see Eq. (5)). Activation energy and pre-exponential factor can be calculated from the slope and y-intercept of the kinetic plot of Eqs. (9) and (10) (linear plot). Trial-and-error method is used to determine the order of reaction in Coats Redfern technique. Note that, the reaction order can be any real number (e.g., n = 0.1, 0.5, 1, 1.5, 2, 3, 5, 10, and so on) and usually determined from the best-fit response. In this work, we began with a small n value and if necessary, increase the value if model failed to give best response (e.g., low R^2 value or negative activation energy).

3. Result and discussions

3.1. Data collection and model development using multiple regression approach

A number of models to predict calorific values of solid fuels have been proposed and the models are either based on

chemical analysis [7, 28], proximate analysis [7, 24, 29, 30], or ultimate analysis [7, 10, 24, 29–31]. Sheng and Azevedo [7] argued that among these three types of models, the most reliable and adequate prediction approach are based on the final analysis. Qian et al. [15] claimed that the equations derived to calculate HHV of biochar from the final study are fairly accurate. HHV prediction accuracies from proximate-based models are moderate because they could only provide an empirical biomass composition. The accuracies of chemical-based models can be quite poor attributable to variation of component characteristics [31]. Our attempt in this work is to come up with a more accurate, reliable, and holistic model to accurately predict calorific values of a wide range BSW and their combinations based on feedstocks' final analysis. In this study, analytical data range used to predict BSW calorific values are:

- Carbon, C (41.6% - 91.6%)

- Hydrogen, H (0.70% - H - 9.70%)

- Oxygen, O (1.00% - 46.5%)

- Nitrogen, N (0.00% - 5.25%)

- Sulfur, S (0.00% - 5.60%)

Calorific values and elemental compositions of 32 biomass feedstocks are gathered through extensive literature reviews [15–22]. These feedstocks are classified into three types: (1) municipal solid waste (MSW), (2) biomass and (3) biochar. One interesting trend to note from the collected data is the volatile matter and fixed carbon goes hand in hand with the calorific values. High volatile matter and fixed carbon content make the solid fuels reactive and easy to be ignited at low temperature resulting in high calorific values. Regardless of feedstocks, higher carbon and hydrogen contents generally imply higher calorific value fuels. An opposite trend of biomass calorific values is observed for solid fuels with high moisture and ash content [32]. Feedstock with high moisture content (50 – 99%) results in lower combustion temperature (418 – 426 °C) and can significantly impact combustion behavior of the system [33]. A relatively accurate correlation is obtained when coefficient of determination (R^2) value is close to 1. Using multiple regression methods, two correlations, namely Correlation A for municipal solid waste sample and Correlation D for biomass and biochar were developed (see Table 1).

Calorific value predictions from the developed models (i.e., Correlation A and D) were compared with calorific values of different solid fuel samples reported in literature (experimentally determined and/or predicted). Accuracies
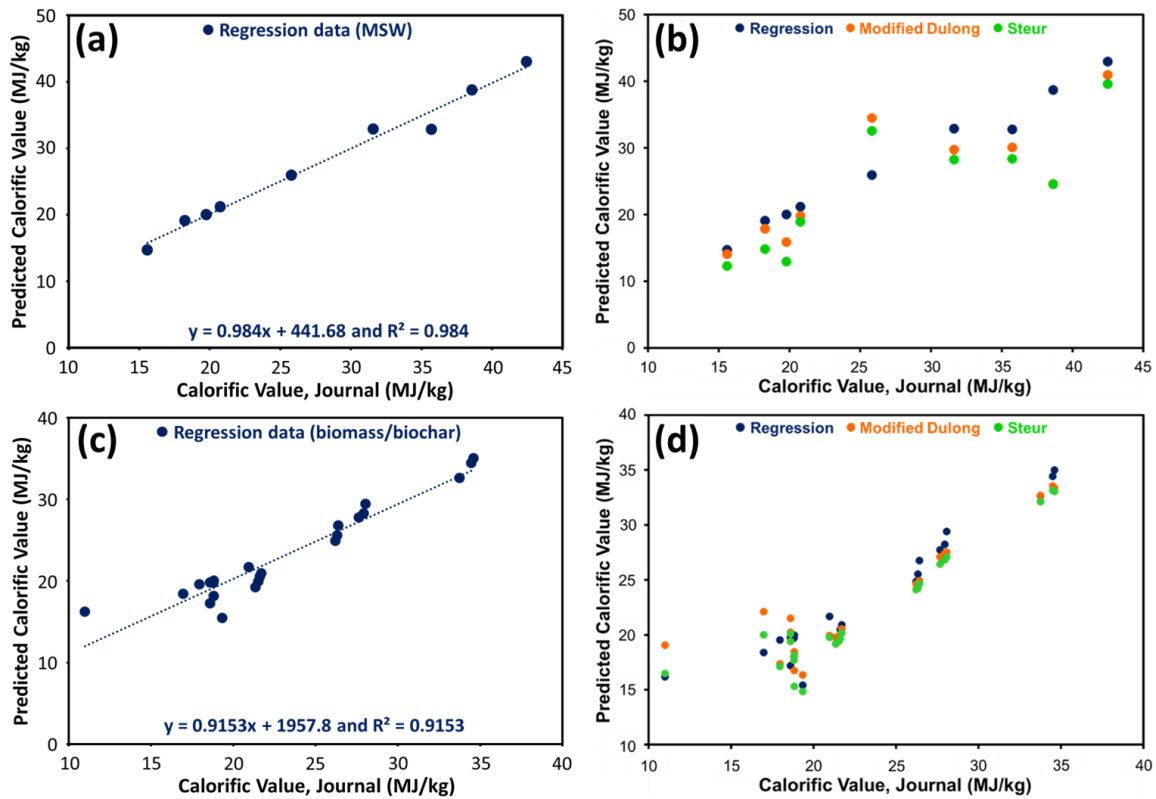
Fig. 1. Regression plot and comparison between predicted and literature calorific values for the regression, Dulong, and Steur correlations based on ultimate analysis for (a – b) MSW sample composition and (c – d) biomass/biochar sample composition.

of the models were also compared with established models such as Dulong and Steur. Performance criteria to select the most optimal models are R^2 coefficient and mean absolute percentage error (MAPE). The R^2 coefficient and MAPE values are widely used in statistical analyses to quantify correlation' accuracies where high accuracy correlations will have low MAPE values and R^2 coefficients closer to 1.

As shown in Fig. 1, the developed models able to predict calorific values of BSW closer to the mainline. The models (i.e., Correlation A and D) in Table 1 have high R^2 coefficients of 0.98 and 0.92 and lower MAPE values of 3.2% and 7.10% for MSW and biomass/biochar samples, respectively (see also Fig. 1(a) and Fig. 1(c)). For MSW samples, Dulong correlation (Correlation B) and Steur correlation (Correlation C) have high MAPE of 14.5% and 20.1%, respectively. Meanwhile, the MAPE of Dulong (Correlation E) and Steur (Correlation F) for biomass/biochar samples are 9.90% and 9.88%, respectively. The equations derived in prior studies (i.e., Dulong and Steur equations) perform poorly as the equations are originally intended specifically for coal samples. In this work, the majority of the samples tested are bio-based where large variations in samples' physico-

chemical properties are to be expected. When compared to coal, biomass usually have lower carbon contents (42 – 54%), higher oxygen contents (35 – 45%), and lower heating values (14 – 21 MJ·kg^{-1}) [29].

3.2. Model validation for solid fuel mixture (comparison with literature data)

Model abilities to accurately predict heating values of different combinatorial scheme of BSW can be assessed from their calculated percentage error. A positive error value indicates an overestimation, while a negative error value indicates underestimation of the calorific value predictions. Models with small percentage error are desirable as the predictions are more accurate. The model (i.e., Correlation A and D) abilities to accurately predict calorific values of different BSW combinations are assessed by comparing the calculated calorific values with those reported in literature. Generally speaking, individual or combination of solid fuels with calorific values of 25 MJ·kg^{-1} is considered as high calorific value fuel sources. For a comparison coal has a calorific value ranging from 23 to 28 MJ·kg^{-1} [33].

Five solid fuel combinations from MSW, biomass,

Table 1. Correlations for predicting the calorific value of MSW, biomass, and biochar.

Formula*	R^2	MAPE (%)	Ref.
$HHV_{pred} = 908.37C + 2942.94H + 4439.73\,S + 518.92O - 63558.52$ (**Correlation A**)	0.98	3.20	THis work
$HHV_{pred} = (80.5C + 338.6H - 42.3O + 22.22\,S + 5.55\,N) \times 4.186$ (**Correlation B**)	0.65	14.5	[34]
$HHV_{pred} = (81C + 342.5(H - O/8) + 22.5\,S - 6(9H + MC)) \times 4.186$ (**Correlation C**)	0.71	20.3	[35]
$HHV_{pred} = 382.62C - 368.16H + 2788.24\,S - 37.83O + 926.26$ (**Correlation D**)	0.92	7.10	This work
$HHV_{pred} = (80.5C + 338.6H - 42.3O + 22.22\,S + 5.55\,N) \times 4.186$ (**Correlation E**)	0.83	9.90	[34]
$HHV_{pred} = (81C + 342.5(H - O/8) + 22.5\,S - 6(9H + MC)) \times 4.186$ (**Correlation F**)	0.85	9.80	[35]

*HHVpred is predicted high heating value in kJ/kg. C, H, O, N, and S represent biomass content in a form of elemental carbon, hydrogen, oxygen, nitrogen, and sulfur, respectively

biochar, and coal categories depicted in Fig. 2(a – b) are used as samples. For MSW category, plastic film, styrofoam, used tires, rigid plastic, rubber, and carpet samples are selected. Meanwhile, for biomass/biochar category, oil palm trunk (OPT) 500, palm kernel shell, coconut fiber, sawdust, and MSW (including food) are selected. It is postulated that the proposed combination will have an attractively high specific energy outputs as opposed to the individual solid fuels. In Fig. 2(a – b), predicted value is defined as effective heating value of solid fuel mixture (1:1 ratio by weight) calculated using the models. On the other hand, literature value is defined as average heating values of two solid fuels mix reported by researchers.

Fig. 2(a) investigate the potential of converting multiple plastic and used tires into solid fuels for energy production. Previous research found that used tires have high calorific values between 29 – 39 MJ·kg^{-1}. In addition, used tires are made up of roughly 90% organic components which make them an excellent type of fuel source [36]. Plastics' calorific values can exceed 40 MJ·kg^{-1} due to their high carbon and hydrogen content with low ash content. Fig. 2(a – b) suggest that the two correlations proposed in this work (i.e., Correlation A and B) perform reasonably well for BSW mixture due to small differences between the predicted values and literature values (average of two individual heating values previously reported by researchers). For MSW, the majority of the data are within 5% error. On the other hand, most of the predicted values for biomass/biochar in Fig. 2(b) are found to be within a 7% margin of error. The percentage error for MSW (food waste included) and biochar (OPT500) mixture however is relatively high (16.90%). As a result, the correlation is limited to biomass/biochar only and does not apply to MSW, which includes food waste. Co-firing biomass/biochar with coal produces relatively high energy outputs, hence a good option to consider for energy production as shown in Fig. 2(b).

3.3. Model validation for solid fuel mixture (comparison with experimental data)

Fig. 3(a – b) shows comparison between experimental calorific values and models' predictions. Solid fuel combinations consisting of two individual BSW 1:1 ratio by weight were determined using bomb calorimeter. The models can predict calorific values of the BSW with reasonable accuracies where most of the data are within ±10% error for MSW except for multiple plastic/textile combination, which is 15.5% error. Meanwhile, the percentage error for biomass/biochar combinations is similar to MSW except for biochar (OPT500)/coal samples with MAPE of 15.04%.

This study showed that combining different biomass solid waste is a good approach to consider as the resulting mixture would have higher effective heating values. Shi et al. [18] demonstrated that combination of textile and used tires yield an effective calorific value of 30.5 MJ·kg^{-1}, 47% higher when compared to burning textile only. Calorific value of palm kernel shell according to Carmo-Calado et al. [17] is 18.8 MJ·kg^{-1}. A 1.5 MJ·kg^{-1} increase in energy output can be obtained by co-firing palm kernel shell with coal. Energy generation efficiency of biomass solid waste co-firing can be relatively high, reaching up to 45% when compared to pure biomass, which is usually less than 30% [37].

3.4. Biomass solid waste combustion behaviors

Fig. 4 shows TG and DTG profiles obtained at a heating rate of 20 °C·min–1 for three BSW combinations: (1) multiple plastic/biochar, (2) used tires/biochar, and (3) used tires/textiles. Thermal behaviors of the samples vary greatly as shown in Fig. 4 (a – c). According to a popular belief, there are three major stages in the combustion process. On the DTG curve, the first region (Stage 1) represents dehydration and water removal process. The second stage is caused by the oxidation and removal of volatile matter in the solid samples (Stage 2). The third region (Stage 3) is produced as a result of the oxidation of the char that remains after removal of the volatiles from the samples
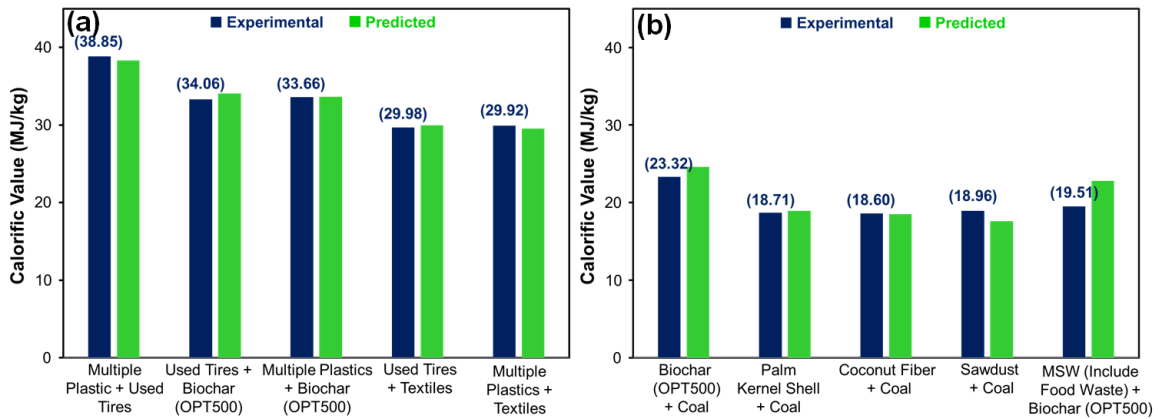
Fig. 2. Summary of the optimized combination sample data used to validate (a) Correlation A for MSW and (b) Correlation D for biomass/biochar mixture.
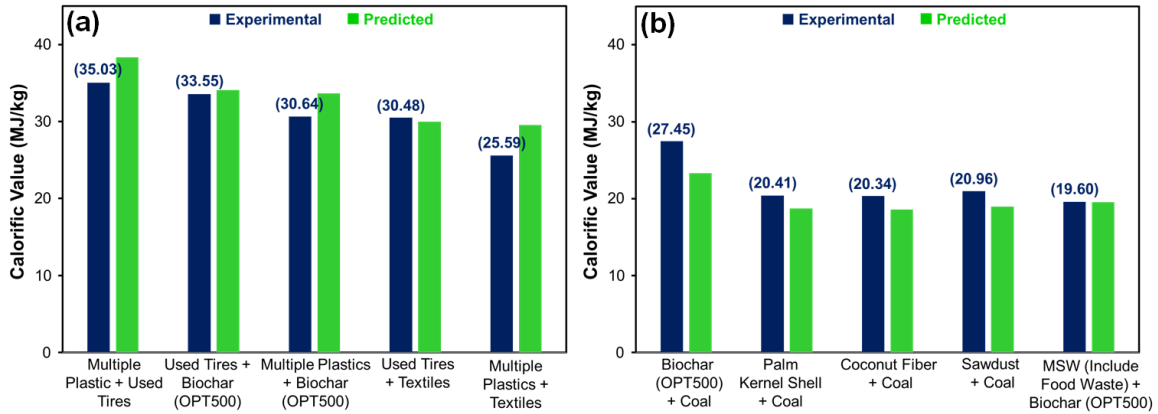

Fig. 3. Summary of the comparison between experimental calorific value and predicted calorific value for five sample combinations of (a) MSW and (b) biomass/biochar combinations.

[38].

The first stage of combustion for multiple plastic/biochar, used tires/biochar, and used tires/textile combinations occur at temperatures ranging from 39 °C – 150 °C, 38 °C – 137 °C, and 45 °C – 142 °C, respectively, attributable to sample dehydration. At intermediate stage, volatile and fixed carbon which constitute the main structure of the multiple plastic/biochar, used tires/biochar, and used tires/textile combinations begin to burn. Used tires/biochar combination have a high ignition temperature due to mixture high thermal stability. As the temperature rises, decomposition rate of the sample increases. The graphs in Fig. 4 show that the samples' mass losses are steadily decreasing, indicating gradual decomposition of organic and volatile materials. At this stage, total mass loss of used tires/biochar mixture is 24.5% while total mass loss of used tires/textile is 43%. The third stage of mass loss of used tires/biochar and used tires/textile combination

begin at 393 °C – 590 °C (with mass losses 65%) and 331 °C – 475 °C (with mass losses 60%), respectively, corresponding to residual char burning process. Beyond final temperature, the variability in the sample mass is undetectable. The phase of mineral decomposition in the air, according to Chen et al. [39] is not visible on the graph.

Important combustion parameter of BSW samples such as ignition temperature (T_i), burnout temperature (T_b), and combustion index (S) can be extracted directly or indirectly from the TG-DTG curve. In this work, T_i is determined using the intersection method, while T_b is identified using conversion method (temperature where sample conversion reaches 99%) [40]. Combustion parameters of the three sample combinations are shown in Table 2. The combination of used tires/textiles mixture has the lowest T_i of 321 °C while used tires/biochar combination have the highest T_i of 381 °C. It is worth mentioning that T_i of used tires/biocar recorded in this study is within a similar tem-
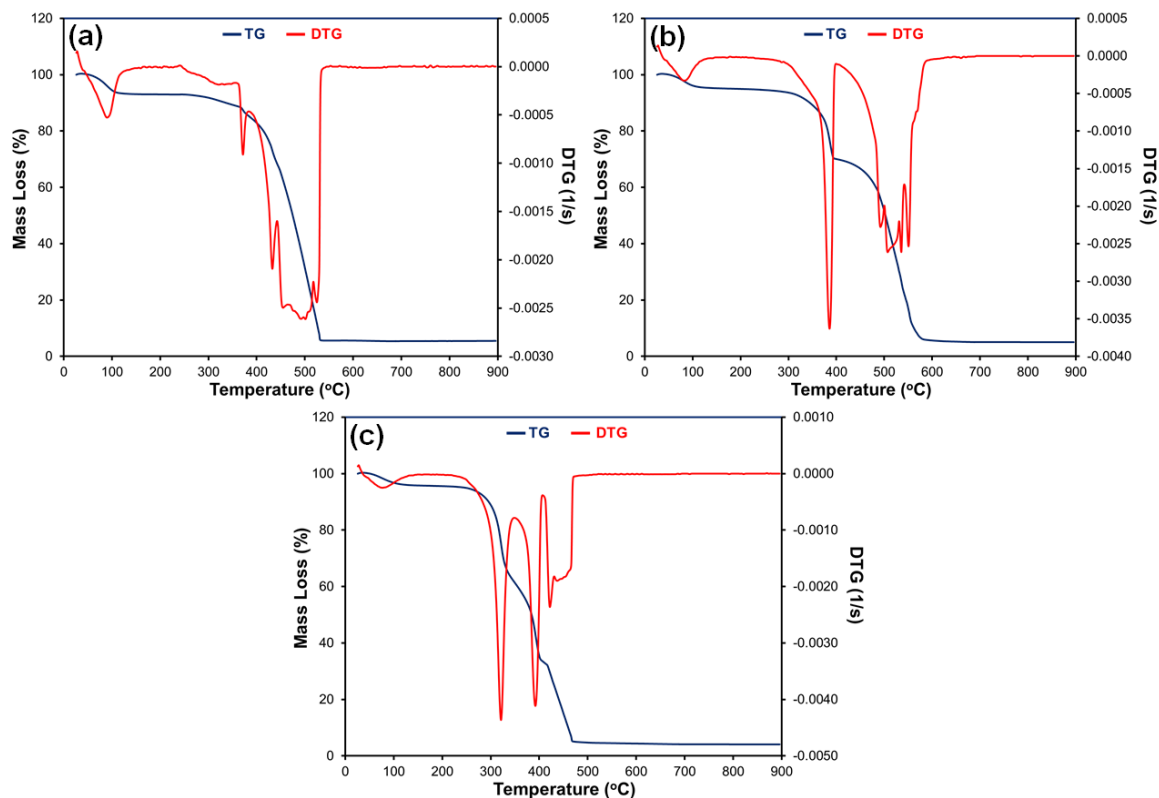
Fig. 4. Comparison of the TG-DTG curves of (a) multiple plastics/biochar (b) used tires/biochar (c) used tires/textile sample combinations.

perature range for used tires/coal combinations reported by Li et al. [41]. T_i is an important index for indicating the combustion property of a BSW mixture where lower T_i indicates better combustion property. T_i is determined by the early releases of volatiles and a rate at which heat is released by volatiles combustion. Vamvuka and Sfakiotakis [26] found that higher oxygen content in the fuel result in faster thermal devolatilization and oxidation. On the other hand, moisture content of the fuel slightly increases ignition and burnout temperatures. Based on collected data, biochar has a higher moisture content, resulting in a higher T_i.

Burnout temperatures of the sample combinations are arranged in the following order: used tires/textile < multiple plastic/biochar < used tires/biochar. In addition to T_i and T_b values, combustion index (S) can also be used to represent samples combustion reactivities (Table 2) where a higher S value indicates better ignitability. S values of BSW samples are ranked in the following order: used tires/biochar < multiple plastic/biochar < used tires/textile, which agrees well with the Ti results. In terms of combustion parameters, the combination of BSW is a reactive fuel, which could be a viable alternative for replacing

Table 2. Combustion parameters for different combinations of BSW at 20 °C ·min⁻¹.

Sample	T_i (°C)	T_b (°C)	S
Multiple plastic/biochar	371	521	3.11×10^{-12}
Used tires/biochar	381	581	8.33×10^{-13}
Used tires/textile	321	468	8.12×10^{-11}

non-renewable energy sources with renewable and clean energy.

3.5. Analysis of combustion kinetic parameters

The corresponding kinetic parameters of three combination of BSW samples are shown in Table 3. Generally speaking, combustion process of the sample mixtures can be divided into three stages as described in the preceding section. Using the Coats Redfern method, the activation energy of multiple plastic/biochar combination ranges from 34.93 kJ·mol⁻¹ – 170.5 kJ·mol⁻¹. Used tires/biochar combination has activation energy in the range of 37.57 kJ·mol⁻¹ – 239.0 kJ·mol⁻¹. Lastly, used tires/textile combination has activation energy in the range of 7.71 kJ·mol⁻¹ – 61.30 kJ·mol⁻¹. It is a well-known that material with low activation energy is more reactive, hence easier to be combusted. Since used

Table 3. Combustion kinetic parameter of the combination of biomass solid waste.

Sample	Combustion stage	Reaction order, n	EA (kJ·mol^{-1})	C (min^{-1})	R^2 value
Multiple plastic/biochar	I	2	41.57	2.75×10^4	0.929
	II	2	34.93	2.15×10^1	0.923
	III	2	170.5	7.58×10^{11}	0.927
Used tires/biochar	I	2	43.70	5.545×10^4	0.948
	II	2	37.57	5.285×10^1	0.925
	III	2	239.0	1.00×10^{16}	0.952
Used tires/textile	I	2	7.710	1.09×10^{-1}	0.979
	II	2	61.31	3.63×10^4	0.946
	III	2	24.93	8.06×10^2	0.955

tires/textile combination has lower activation energy, it is therefore more flammable. From Table 3, activation energy for multiple plastic/biochar and used tires/biochar combination in the second stage is lower than that of other stages, reflecting the diffusion-based volatile release phase [14]. Residual carbon after the second stage is more difficult to burn and requires more energy to pass through the process. It is therefore not surprising that the third stage has the highest activation energy among others.

4. Conclusions

In this work, two predictive models of calorific values for biomass solid waste were developed through extensive literature survey followed by regression method. The models were accurate in predicting specific energy outputs of a wide variety of solid fuels with R^2 coefficients of 0.98 and 0.92 for municipal solid waste and biomass/biochar, respectively. The models also have low MAPE values of only 3.2% for municipal solid was and 7.10% for biomass/biochar outperforming other commonly reported correlations (i.e., Dulong and Steur). The predicted calorific values of the biomass solid waste combinations were validated by comparing them with experimentally determined calorific values. The model predictions agree well with the experimental results within a MAPE of less than 15%, indicating excellent prediction accuracies and general applicability of the models. Important key combustion parameters of the biomass solid waste combinations such as ignition temperature, burnout temperature, and maximum peak temperature were retrieved from gravimetric analysis, and then correlated with combustibility indices. The two models developed in this work could be important to predict calorific values of a wide variety of solid fuels and their combination with high degree of accuracy. Moving forward, we recommend adopting a more sophisticated analysis tools such as machine learning and data mining to ensure model robustness when transitioning to a more complex biomass mixture.

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