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Investigation of the chemical exergy of torrefied biomass from raw biomass by means of machine learning

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ABSTRACT

Torrefaction is one of the most important pretreatment processes to improve the quality of biomass as fuel and overcome its disadvantages. Predicting the chemical exergy of torrefied biomass is essential for evaluating and optimizing the performance of biocoal-based power plants. Therefore, the authors report on a wide range of research that has been conducted to accurately measure the chemical exergy of solid fuels. Nowadays, many researchers are working on computational methods to reduce the number of actions in experimental research. However, until now, researchers have not presented a model that predicts the chemical exergy of torrefied biomass considering the experimental conditions. This study is novel in two ways: first, the exergy of torrefied material was calculated using parameters of torrefaction conditions prior to the torrefaction process. Second, the developed model ANN predicts the chemical exergy of torrefied material directly from the results of proximate analysis of raw biomass samples. Statistical performance indicators show that the predictive capacity of the ANN model is satisfactory. The R^2 value was greater than 0.92 for training and 0.79 for testing, while the MAPE value was less than 4% for both training and testing.

1. Introduction

Energy-related economic and environmental concerns increasingly affect the entire world, and preventing these issues is critical for a sustainable future. The use of fossil fuels generates significant problems on a worldwide scale, such as pollution, poisonous gas emissions, and climate change due to greenhouse gases, etc. Considering that fossil fuels satisfy nearly 80% of total energy consumption [1], putting alternative energy productions into practice on large scales is even more important in our modern world. Therefore, in recent years, there has been a greater focus on clean and renewable energy technologies, and research on long-term solutions have been conducted [2].

After oil, coal, and natural gas, biomass is the most commonly utilized fuel, accounting for around 10% of annual energy consumption [3]. Biomass energy appears to be an alternate solution with significant potential to replace fossil fuel resources and push humanity closer to a sustainable energy future [4]. It can be simply described as a renewable energy source that is derived from organic materials found in nature, is abundant and widely available, produces low greenhouse gas emissions, is carbon neutral, and is biodegradable [5]. Biochemical and thermochemical cycles can be used to convert biomass into raw chemicals, and it can also be employed as a solid, liquid, or gaseous material [6]. However, due to some major drawbacks of biomass, such as high moisture content, varying quality and calorific value, the need for a huge area for stockpiling, relatively low energy density, and financial issues related to transportation and distribution, its use on a large scale is limited [7,8]. Consequently, in order to improve energy quality, a pretreatment procedure for raw feedstock appears to be necessary.

The most common processes are thermochemical pretreatments such as torrefaction, carbonization, gasification and pyrolysis [9]. Torrefaction is a mild pyrolysis process that occurs at temperatures between 200 and 300 °C in an inert medium. Along with the inert atmosphere, a small quantity of oxidative atmosphere is used in the definition of torrefaction [10–12]. The procedure has a slow heating rate (<20 °C/min), and the residence duration might range from a few minutes to 3 h [13]. At the completion of the torrefaction process, biomass is purified from moisture and light volatiles, fibrous structures are partially destroyed, energy density, grindability, and homogeneity increase, and the physicochemical characteristics of the fuel alter significantly [14]. Torrefaction also improves the C:O and C:H atomic ratios, as well as reactivity. Hereby, there is a lot of profit in terms of energy efficiency, stockpiling, shipping, and disposal [15–17].

In addition to adopting alternate energy sources, it is crucial to

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Nomenclature

ANN	Artificial neural network
DAF	Dry ash-free
DB	Dry basis
FFNN	Feed-forward neural network
FC	Fixed carbon
HHV	Higher heating value
MAPE	Mean absolute percentage error
MSE	Mean squared error
VM	Volatile matter
WT	Weight

increase the process performance [18]. Especially for biomass-based power plants, it is important to contain efficient technologies that can compete with fossil fuels [19]. Efficiency, however, may be perceived in a multitude of ways, and its comprehension is guided by a variety of factors [20]. Exergy analysis is one of the most extensively used methodologies for assessing system performance and energy quality. The maximal amount of work that can be done to bring a system into equilibrium with its surroundings is described as exergy [21]. There are many forms of exergy such as mechanical, kinetic, potential, chemical, heat, and radiation, etc. [18]. However, exergy is generally investigated under two groups in the name of physical exergy and chemical exergy. If a change in the system does not result in a chemical difference, it is considered as physical exergy; nevertheless, when there is a change in the structure of the materials and a chemical reaction occurs, it is considered as chemical exergy. The physical exergy of biomass is usually assumed to be zero [22].

The minimal energy necessary to synthesize a pure chemical substance at the surrounding reference state from its constituent elements in the identical circumstances is referred to as chemical exergy. The calculation is divided into two stages: first, the reactants interact to generate non-reference state products, and then the products are brought into the reference state [21]. A pressure of 1.01325 bar and a temperature of 25 °C are conservatively assumed to represent the reference condition. If the fuel is in a liquid or gas phase and its chemical composition is known, chemical exergy value can be obtained from the tables [23]. However, evaluating the chemical exergy of a carbon-based solid material is difficult due to its vast diversity, complicated structural interactions, and uncertain thermodynamic properties [24]. Moreover, due to the restricted data for organic structures in biomass, the correlations might not be applicable to all kinds of biomass. Therefore, some assumptions and simplifications are applied.

The standard molar chemical exergy values have been determined using a variety of techniques. Rant [25] proposed a correlation in the chemical exergy calculation for solid and liquid fuels for the first time; however, correlation contains a constant coefficient for the proportion of the chemical exergy to the heating value. Further, Szargut and Styrylska [26] demonstrated that the ratio is significantly dependent on the structure of the fuel; however, due to a lack of associative thermodynamic data, the correlations are difficult to utilize and do not include the influence of elemental sulfur. Shieh and Fan [27] proposed a model for structurally complex materials but in the model entropies of the products and reactants are considered to be similar in an oxidation reaction, which is erroneous in real-world applications. Models for forecasting chemical exergy of solid fuels were established by Stepanov [28] and Kaygusuz [29], but their calculations are confined to specific materials and hence cannot be utilized extensively.

In addition to mathematical correlations, machine learning algorithms have also been developed to calculate chemical exergy [30,31]. Artificial neural networks (ANNs), a subset of machine learning, are frequently used to simulate complex and nonlinear tasks with numerous input variables. ANNs do not provide a theoretical or physical clarification [32], and classified as black-box models [33]. As a result, ANNs can be used to create a model that simulates the experimental torrefaction process and calculates the chemical exergy of the torrefied material.

In this study, the chemical exergy values of torrefied biomass materials were estimated from raw biomass without performing an experimental torrefaction procedure. Previous studies have predicted the chemical exergy of torrefied materials [34–37], but all these works include the calculations using the experimental procedure. However, no work has yet been published on estimating the chemical exergy of torrefied biomass from raw biomass. The strategy used in this work overcomes the modeling limitations for the torrefaction process and improves accuracy under a wide range of operating conditions. This modeling approach also directly estimates the chemical exergy without requiring physicochemical parameters of the torrefied material, such as calorific value and elemental composition, which are essential for calculating the chemical exergy of a solid fuel. Consequently, it provides a shortcut for complex procedures. This is the first study to establish a model for predicting the chemical exergy of torrefied biomass based on the operating parameters and the results of proximate analysis of raw biomass.

2. Methodology

The theoretical-scientific background and practical formulations of the techniques used in this study are summarized in the Methodology section. This section explains the literature review and the creation of the dataset, the chemical exergy calculations, the mathematical basis of ANN, and the statistical performance evaluation.

2.1. Samples

A comprehensive survey was performed as part of the literature review process. It was ensured that no information about the oxy-torrefaction process was included throughout the data gathering process. The physicochemical characteristics of torrefied material, torrefaction duration and temperature, and the results of proximate analysis of lignocellulosic raw biomass were compiled from 37 independent works to create a dataset. Subsequently, the chemical exergy of the torrefied biomass was determined based on the HHV and elemental composition (Section 2.2). The Supplementary data (Appendix A) information presents the operating parameters for torrefaction processes and the physicochemical properties of torrefied material and raw lignocellulosic biomass. While most studies determined the HHV of torrefied biomass by experiments, Lam et al. [38], Singh et al. [39], Tong et al. [40], Bai et al. [41], Tian et al. [42], Wannapeera et al. [43], and Pala et al. [44] quantified HHV using correlations.

2.2. Exergy calculation

According to the chemical exergy definition, the sample's standard molar chemical exergy is nearly similar to the standard molar Gibbs free formation energy. The bonds between the reactants are broken, and the atoms and electrons rearrange to form products in a chemical reaction. In a combustion process, all combustible constituents in the fuel are oxidized, and products of combustion are formed. The most common substances in a solid fuel are C, H, O, N, S, and Cl, and they are oxidized to form CO_2, H_2O, N_2, SO_2, and HCl [45].

The combustion reaction is represented as follows for 1 kg of dry and ash-free (DAF) solid fuel:

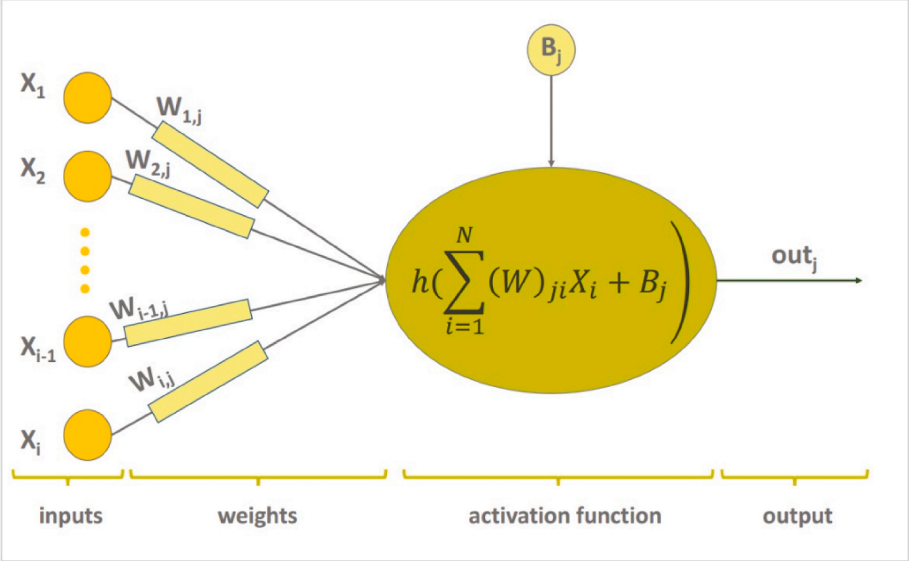


Fig. 1. Architecture of a perceptron.

$$(cC + hH + oO + nN + sS) + \mathscr{V}_{O_2}O_2 \rightarrow \mathscr{V}_{CO_2}CO_2 + \mathscr{V}_{H_2O}H_2O + \mathscr{V}_{SO_2}SO_2 + \mathscr{V}_{N_2}N_2 \quad (1)$$

where c, n, s, o, and h referring to the molar number of C, N, S, O, and H in per kg sample (DAF). The molar numbers of all the substances in the combustion without oxidation of nitrogen are calculated by:

$$\mathscr{V}_{CO_2} = c,\ \mathscr{V}_{H_2O} = \frac{1}{2}h,\ \mathscr{V}_{SO_2} = s,\ \mathscr{V}_{N_2} = \frac{1}{2}n,\ \mathscr{V}_{O_2} = c + \frac{1}{4}h + s - \frac{1}{2}o \quad (2)$$

Chemical exergy of solid material e_{DAF}^{CH} is a function of molar chemical exergies of solid material constituents ($\bar{e}^{CH}$), specific absolute entropy of DAF solid material (s_{DAF}), higher heating value $(HHV)_{DAF}$, molar entropy ($\dot{s}$), and ambient temperature (T_0).

Consequently, the equation follows:

$$e_{DAF}^{CH} = (HHV)_{DAF} - T_0[s_{DAF} + \mathscr{V}_{O_2}\dot{s}_{O_2} - \mathscr{V}_{CO_2}\dot{s}_{CO_2} - \mathscr{V}_{H_2O}\dot{s}_{H_2O} - \mathscr{V}_{SO_2}\dot{s}_{SO_2} - \mathscr{V}_{N_2}\dot{s}_{N_2}] + \left[\mathscr{V}_{CO_2}\bar{e}_{CO_2}^{CH} + \mathscr{V}_{H_2O}\bar{e}_{H_2O}^{CH} + \mathscr{V}_{SO_2}\bar{e}_{SO_2}^{CH} + \mathscr{V}_{N_2}\bar{e}_{N_2}^{CH} - \mathscr{V}_{O_2}\bar{e}_{O_2}^{CH}\right] \quad (3)$$

The heating value of a solid material $(HHV)_{DAF}$ can be predicted in MJ/kg in the absence of a measurable value [46]:

$$(HHV)_{DAF} = [152.19H + 98.767]\left[\left(\frac{C}{3}\right) + H - \frac{(O-S)}{8}\right] \quad (4)$$

where S, O, C, and H are the mass fractions of the solid fuel.

The absolute entropy (s_{DAF}) for solid fuel is predicted, in kJ/(kg.K) [47]:

$$s_{DAF} = c\left[37.1653 - 31.4767e^{\left(-0.5646\frac{h}{c+n}\right)} + 20.1145\frac{o}{c+n} + 54.311\frac{n}{c+n} + 44.6712\frac{s}{c+n}\right. \quad (5)$$

where c, o, n, h, and s are the molar mass fractions (kmol/kg) of components in the DAF solid fuel.

Herewith, the specific chemical exergy of solid fuel is predicted, in MJ/kg [48]:

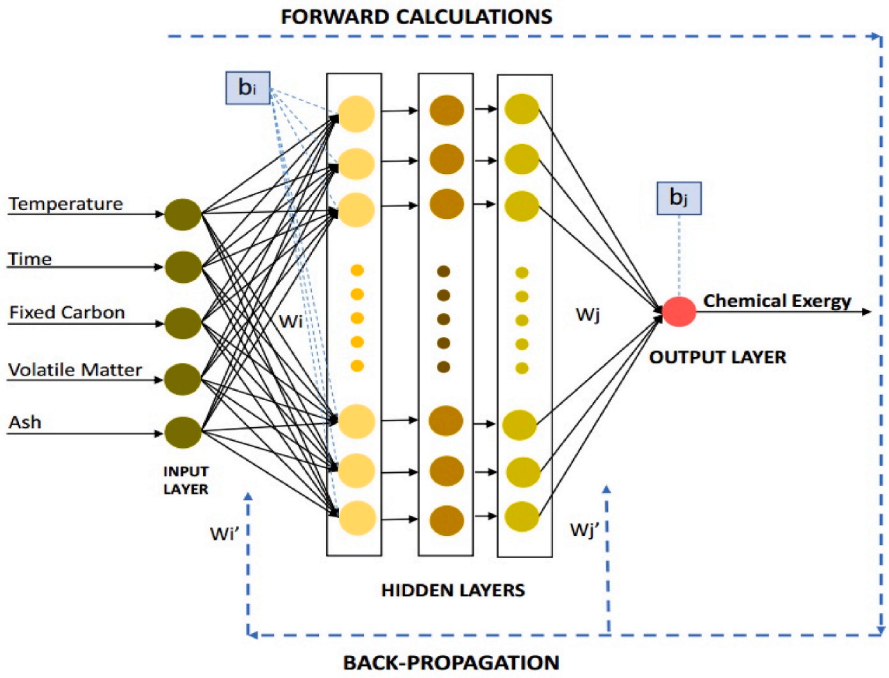


Fig. 2. The ANN design that was employed to calculate chemical exergy.

$$e^{CH} = m_{DAF}\left[\frac{kg(DAF)}{kg(Total)}\right]e^{CH}_{DAF} + m_l\left[\frac{kg(H_2O)}{kg(Total)}\right]e^{CH}_{H_2O} \tag{6}$$

where m_{DAF} denotes the mass fraction of solid fuel and m_l denotes the mass fraction of raw solid material moisture content.

2.3. Artificial neural network

An ANN is a deep sequencing data processing network that mimics the brain and nervous system by simulating the operations of neurons using perceptron [49]. ANN models learn from prior events and establish a pattern to generate the desired result [50]. The computations and output generation are performed by the perceptron, which is the ANN's main processing unit. It can be implemented in a variety of forms. Fig. 1 depicts the overall architecture of a perceptron.

The input (X_i) from the preceding layer neuron's output (out_j) is multiplied by its weight (W_{ji}). The outcomes of multiplications are then summed together with bias (B_j). The starting biases and weights are usually chosen at random. Eq. (7) is used to express a perceptron's output:

$$out_j = h\left(\sum_{i=1}^{N} W_{ji}X_i + B_j\right) \tag{7}$$

where h is the transfer (activation) function. Different types of transfer functions are available, such as logistic, tanh, reLU, ELU, and so on. Three separate activation functions were employed in this study, which can be stated as follows:

$$SELU(x) = \lambda\begin{cases} x, & if\ x > 0 \\ ae^x - a, & otherwise \end{cases} \quad \text{where } \alpha \text{ is } 1.67 \text{ and } \lambda \text{ is } 1.05 \tag{8}$$

$$reLU = \max(0, x) \tag{9}$$

$$ELU(x) = \lambda\begin{cases} x & x \geq 0 \\ a(e^x - 1) & x < 0 \end{cases} \tag{10}$$

Table 1
The features of the ANN model.

Learning parameter	Value
Optimizer	Adamax
Metric	Mean absolute percentage error
Loss function	Mean squared error
Training parameter	**Value**
Validation split	0.2
Test size	0.2
Batch size	10
Epochs	1000

2.4. Performance evaluation

The network error is measured by the difference between the expected and actual values. R^2 (coefficient of determination) in Eq. (11), MSE (mean squared error) in Eq. (12), and MAPE (mean absolute percentage error) in Eq. (13), are the criteria used to forecast chemical exergy from data.

$$R^2 = 1 - \frac{\sum_{i=1}^{n}\left(Y_{predicted} - Y_{actual}\right)^2}{\sum_{i=1}^{n}\left(Y_{predicted} - Y_{mean}\right)^2} \tag{11}$$

$$MSE = \frac{1}{n}\sum_{i=1}^{n}\left(Y_{predicted} - Y_{actual}\right)^2 \tag{12}$$

$$MAPE = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{Y_{actual} - Y_{predicted}}{Y_{actual}}\right| \tag{13}$$

where "$Y_{predicted}$" is the generated value by the ANN, "Y_{actual}" is the target value, "Y_{mean}" is the average value of target outputs, and "n" is the number of instances.

3. Results

In this part, the parameters of the developed ANN model are addressed, followed by the distributions and correlations of the input/output data, and finally the scientific rationale for the dataset and the domain in which the ANN model can be implemented. Finally, the R^2, MSE, and MAPE values obtained in estimating the chemical exergy of

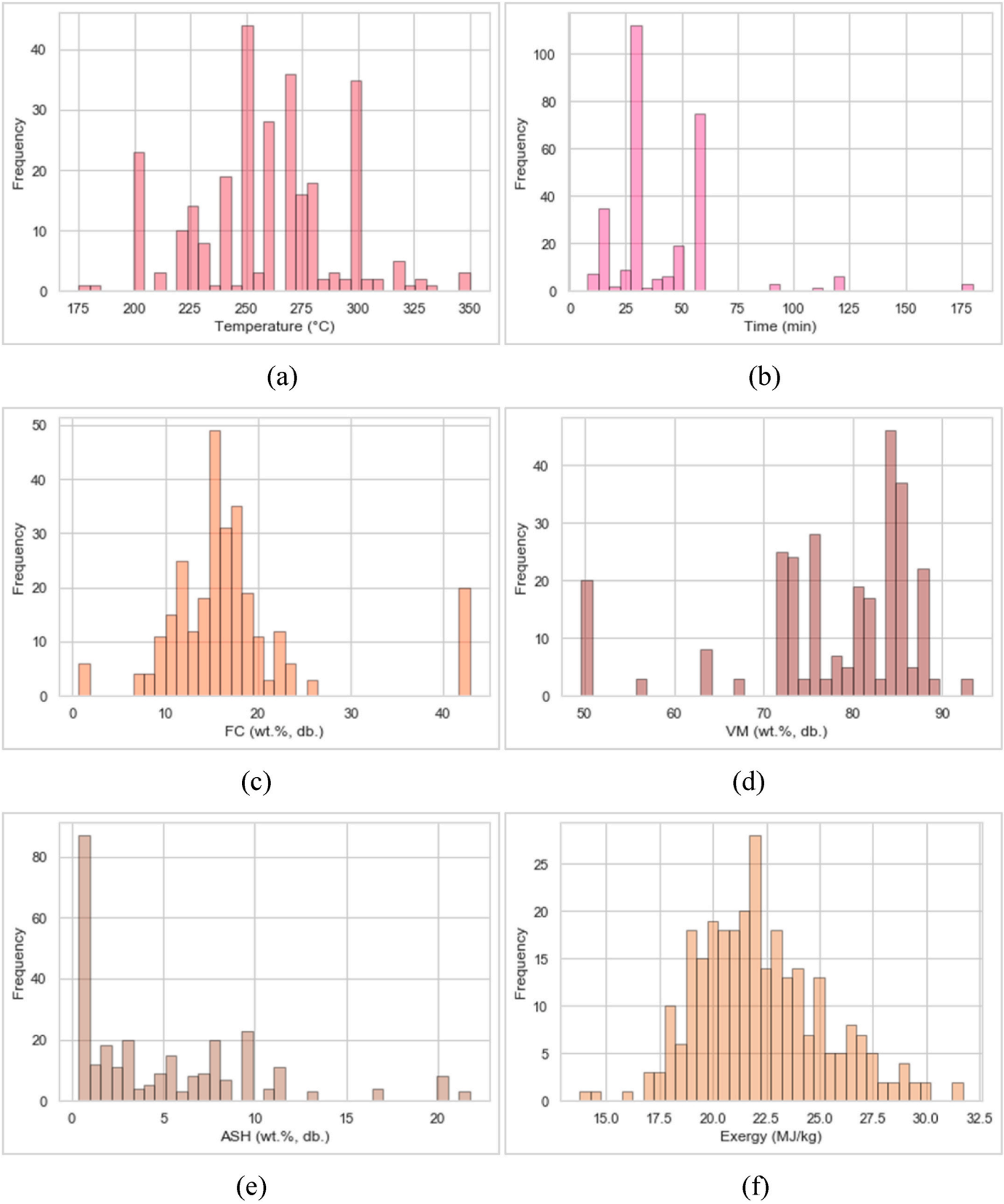
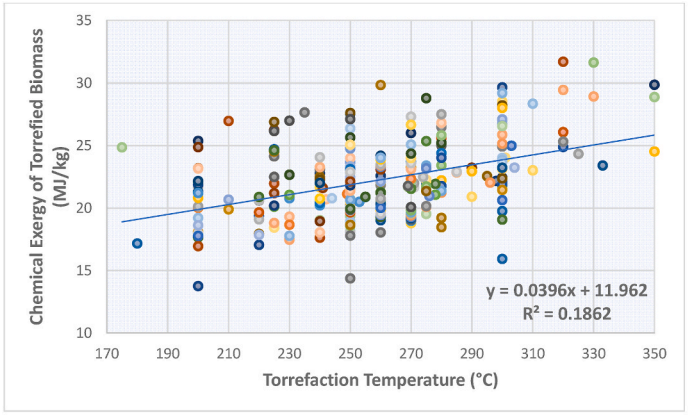
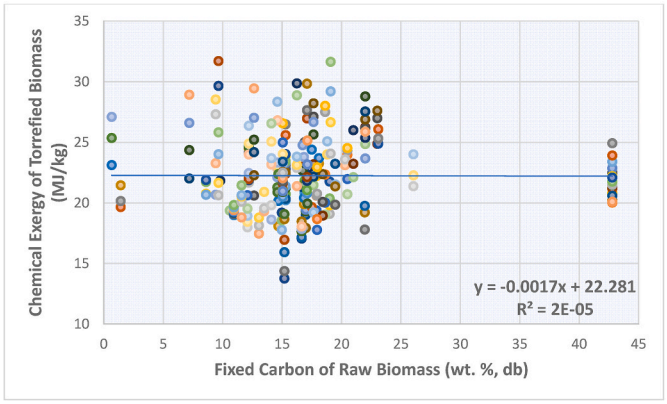


Fig. 3. Histograms of features and label in the dataset: (a) Temperature, (b) Time, (c) FC, (d) VM, (e) Ash, (f) Exergy.



(a)



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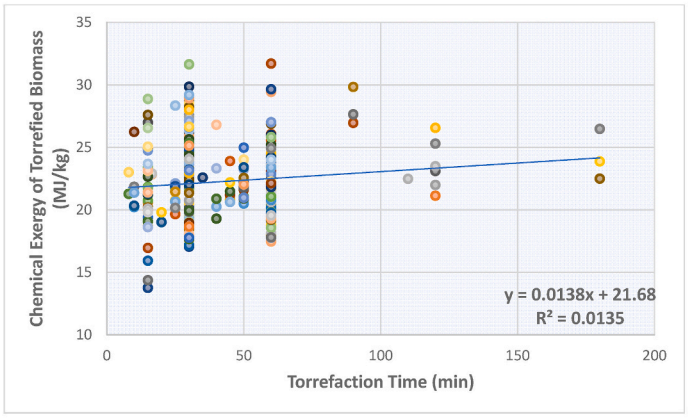

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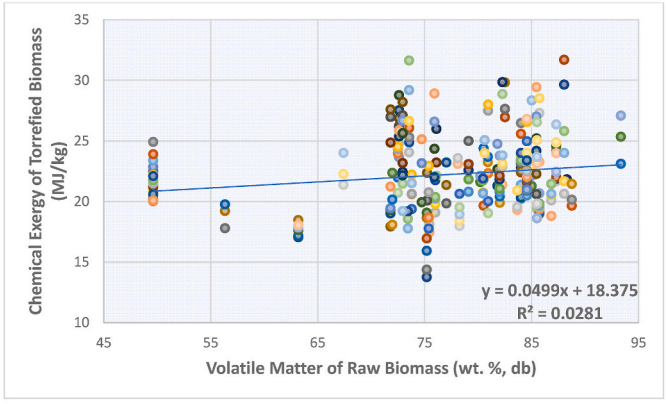
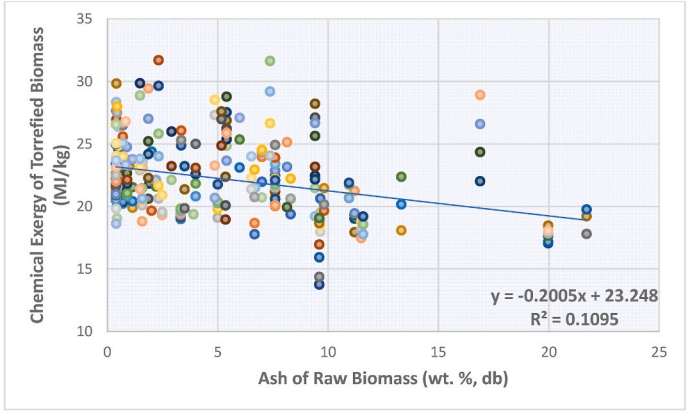


(d)



(e)

Fig. 4. Effect of input variables on chemical exergy: (a) Temperature, (b) Time, (c) FC, (d) VM, (e) Ash.

torrefied biomass samples are evaluated.

3.1. ANN model structure

The architecture (number of layers), topology (connective pattern, feed-forward or recurrent, etc.) and learning regime of neural networks are used to characterize them [51]. There are many types of neural networks that may be used to create a model, but the FFNN (Feed-Forward Neural Network) is the most prevalent in chemical engineering applications [52]. In network forward computation, the signal passes from input to output. The discrepancy in the signal produced in the output layer causes an error signal in the backward flow, returning to readjust bias and weight until the convergence conditions are met. As a consequence, the ANN's effectiveness improves, and it now generates correct predictions for new cases. FFNNs typically have an input layer and an output layer, and one or more hidden layers with interconnected perceptrons. As there is no conventional technique for determining the number of perceptrons and hidden layers, these parameters are calculated by trial and error to verify that the error is as minimal as reasonable. The "TensorFlow" open-source library in Python was used to code the ANN used in this work. Fig. 2 depicts the architecture of the proposed ANN used in this work. The input layer contains five parameters: temperature (°C), time (min), FC (fixed carbon), VM (volatile matter), and ash on dry basis. Hidden layers with 200 neurons in the first layer, 300 neurons in the second layer, and 100 neurons in the third layer receive the input values. Each neuron provides a bias to the outcome after multiplying a weight by the receiving input set. The model receives batch size of 10 input data in this study. Different activation functions

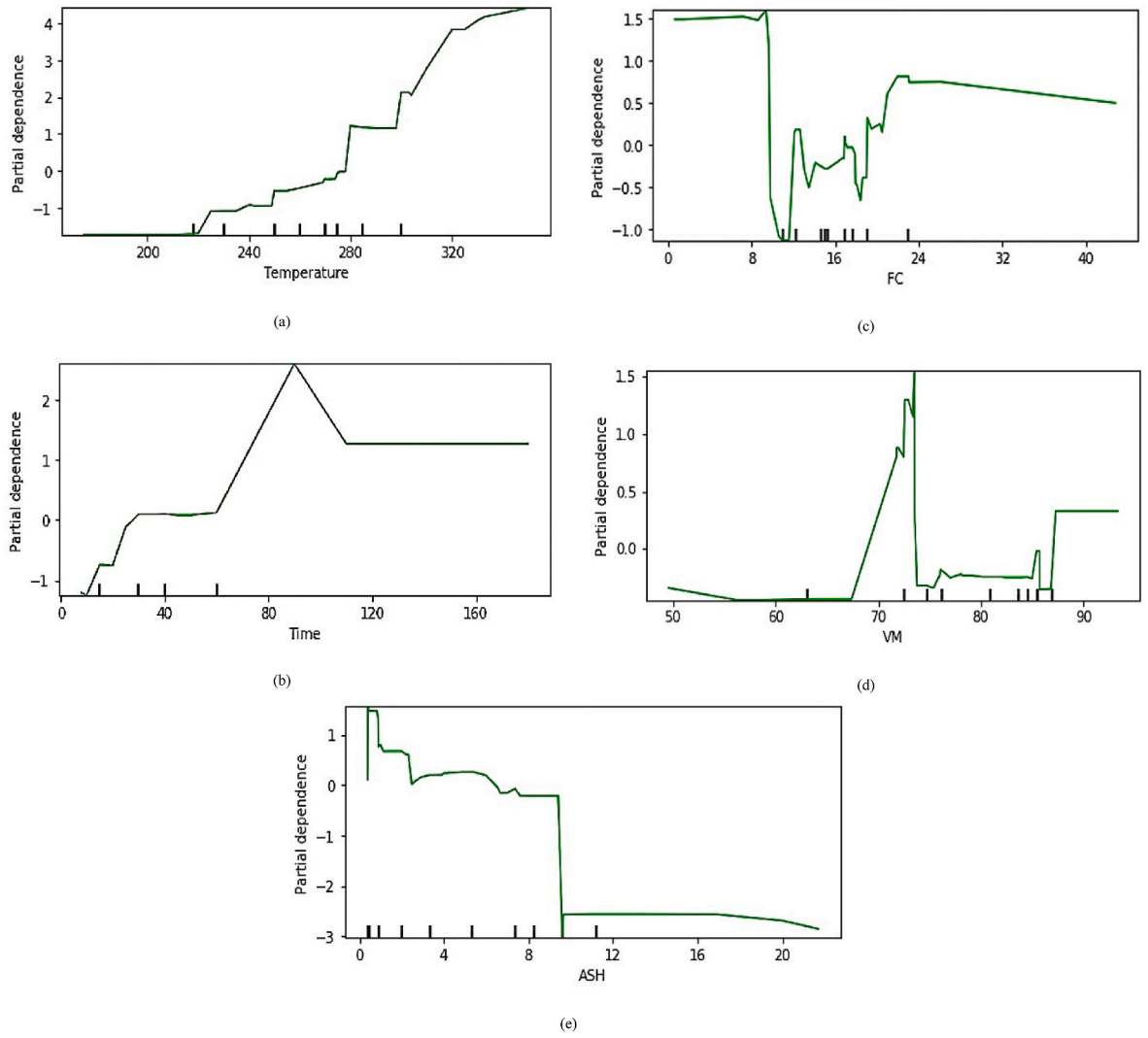


Fig. 5. Partial dependence plots of chemical exergy prediction (a) Temperature, (b) Time, (c) FC, (d) VM and (e) Ash.

were preferred in each hidden layer; ELU, SELU, and reLU functions were selected for the first layer, second layer, and third layer, respectively.

The evaluated information from the hidden layers is sent to the output layer, which calculates the chemical exergy. The model's attributes were adjusted with epochs using an optimizer in order to reduce the value generated by the loss function. An optimizer is an algorithm that controls how the weights of the network are modified in response to the output of the loss function. The Adamax optimizer was chosen for this study's examination. Furthermore, the mean squared error was selected as the loss function and the mean absolute percentage error was chosen as the metric. Table 1 summarizes the features of the ANN model.

3.2. The statistical investigation of the dataset

Using the available studies, a database of chemical exergy of torrefied biomass was established, which includes 284 samples. Chemical exergy (output), torrefaction temperature, torrefaction duration, ash, VM, and FC values of raw material are all included in each dataset. The raw material's proximate analysis findings are presented on a dry basis (wt.%), and the relevant conversions have been used for results reported on a different basis. Chemical exergy values of torrefied biomass samples were calculated using the equations (Section 2.2) in Bilgen and Kaygusuz's study [20]. Mass fraction percentages for the proximate analysis results are in the range of 0.67%–42.79%, 49.61%–93.34%, and 0.39%–21.71% for FC, VM, and ash, respectively. In terms of lowering biased outputs, the proximate analysis findings of raw biomass samples are on a vast scale. Percentages of average weight fractions for FC, VM, and ash are 17.28%, 77.72%, and 4.96%, respectively. Fig. 3 depicts the histograms of the features and the label.

Torrefaction operations with durations of 15 min, 30 min, 45 min, and 60 min are often mentioned in the literature. Aside from these times, longer or shorter torrefaction periods may be observed, depending on the study's subject. As demonstrated in Figs. 3, 30 min (first peak) and 60 min (second peak) appear to be the most typical durations in the dataset. There are tiny peaks at 90 min, 120 min, and 180 min. When the temperature profile is examined further, it is determined that the operating temperature range is primarily divided into three torrefaction conditions: light torrefaction (~ 200 °C), mild torrefaction (~ 250 °C), and severe torrefaction (~ 300 °C) [53–55]. Additionally, the average temperature is 259.64 °C, with a standard deviation of 32.78, demonstrating that the dataset includes the various stages of torrefaction. Torrefied biomass samples' chemical exergy appears to be centered between 20.11 MJ/kg and 23.99 MJ/kg. Although the low standard deviation (3.01) indicates that torrefied lignocellulosic biomasses have similar chemical exergy, there are also outliers such as 13.75 MJ/kg and 31.70 MJ/kg. As a result, the dataset includes a diverse array of lignocellulosic biomass samples with proximate analysis results. Temperatures and durations of torrefaction were selected as frequently preferred values from studies published in the literature. Hence, without

employing an experimental procedure, the torrefaction process can be modeled using this dataset and the ANN model.

3.3. Effect of input variables on chemical exergy

Regarding the input variables, the parameters that most influence the biomass torrefaction process were chosen. Considering that the torrefaction process is the thermolysis procedure that takes place under an inert atmosphere, temperature, residence time and fuel characteristics appear to be the most suitable variables.

The input variables of the ANN model are as follows:

- Torrefaction temperature: The temperature for the torrefaction process. It affects the mass of volatile matter in biomass and chemical bonds to be cracked.
- Torrefaction time: The average amount of time that a solid fuel stays under operating conditions.
- FC: The solid carbon in the fuel that remains in the char in the torrefaction process after devolatilization.
- VM: The condensable and non-condensable vapor released when the biomass is heated. Its amount and composition highly depend on the rate of heating, the temperature, and the residence time.
- Ash: The inorganic solid residue left after the biomass is completely combusted.

The physicochemical characterization of solid fuels, such as biomass, is critical because it allows for the detection of the fuel's energy content as well as the determination of its safe and efficient employment [56]. Simple procedures and ordinary equipment can be used to obtain the findings of proximate analysis, whereas complex methods and specific apparatus are used to determine the results of ultimate analysis [34,57]. Also, the ultimate analysis procedure need the involvement of a highly skilled analyst, although the proximate analysis procedure can be applied by an authorized scientist or engineer. Therefore, the preference of proximate analysis results as input variables is a convenient alternative and facilitated the use of ANN model. Fig. 4 visualizes the effect of input variables on chemical exergy of torrefied material.

The decomposition of organic compounds is caused by the heat absorbed by biomass material. Several volatile compounds (carbonyl groups, aromatic rings, carboxyl groups, methoxyl groups, etc.) are generated during this activity [58]. Higher heat absorption leads to the cracking of stronger organic compounds and the synthesis of more volatile substances. Thus, as the temperature increases, the amount of H and O in torrefied biomass decreases. The torrefied product has a higher C/O and C/H ratio, as well as a higher HHV, due to the removal of water, carbon dioxide, and other light volatiles. In other words, the increase in the O/C ratio in the solid fuel results in a decrease in HHV. When a solid fuel is combusted in air, the HHV offers quantitative information on the overall energy content of the solid material, taking into account the latent heat inherent in the water vapor. As a result, the HHV represents the greatest amount of energy that can be extracted from a specific biomass source.

According to Bilgen [20] and Chen [47], the chemical exergy was significantly related to O/C and H/C ratios. They stated that high levels of H and O reduce the solid fuel's exergy value. Many researches have also claimed that increasing the torrefaction temperature and residence period increases the energy content of solid fuel [43,59–62]. Thus, the increase in temperature and time during torrefaction process is observed as a growth in chemical exergy, as presented in Fig. 4. As the ash and moisture content of the solid fuel increases, the amount of combustible material per unit mass decreases, resulting in a decrease in chemical exergy. Because ash is present in such small quantities in biomass, the effect of inorganic elements in the form of ash chemical exergies, as well as the entropy change in ash generation, may be disregarded [23]. However, it should be noted that there are few studies on the chemical exergy of inorganic matters in solid fuels [24]. Since volatile substances

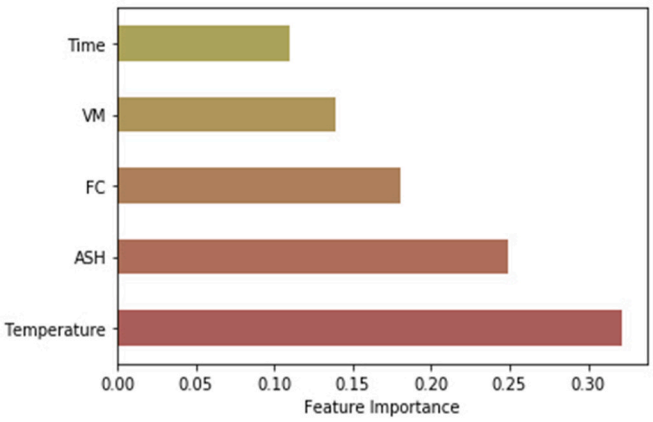
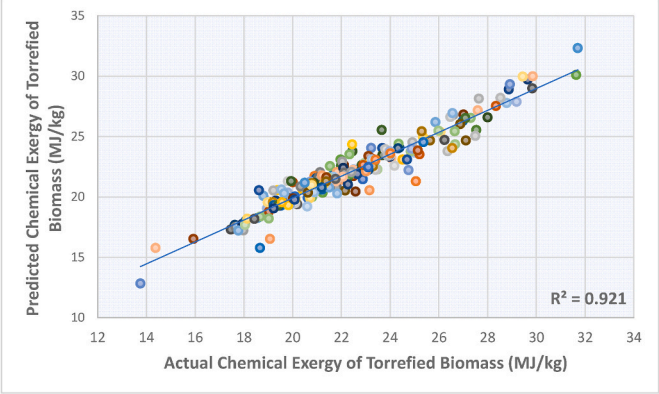
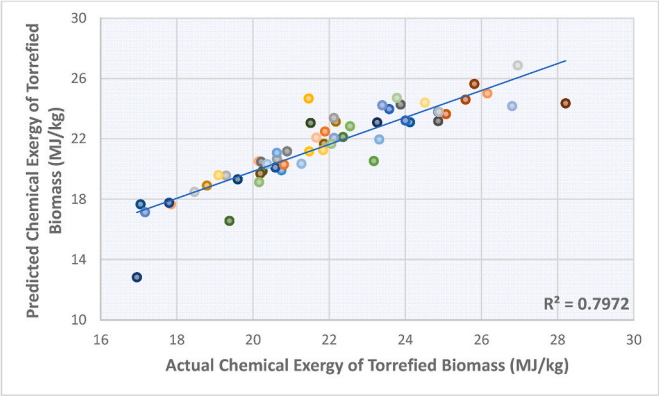


Fig. 6. The contribution of features for the chemical exergy prediction.



(a)



(b)

Fig. 7. R^2 scores for the training (a) and the test (b).

detach from solid fuel and ash is present in small quantities, FC content rises dramatically at the termination of the torrefaction process compared to raw material [17]. The enrichment of C content in the fuel and the increase in heating value result in a growth in the chemical exergy. When Fig. 4 is examined, it is not possible to mention a strong correlation between any input variable and the chemical exergy of torrefied biomass. In addition, partial dependency graphs were used to demonstrate the impact of input variables and their interactions on chemical exergy of torrefied biomass, as illustrated in Fig. 5.

The partial dependency plot depicts the marginal impact of one or two variables on a machine learning model's anticipated result [63]. It can be used to determine if the correlation between the target and a variable is linear, monotonic, or complicated. Increasing temperature and time resulted in the increase in chemical exergy, which was

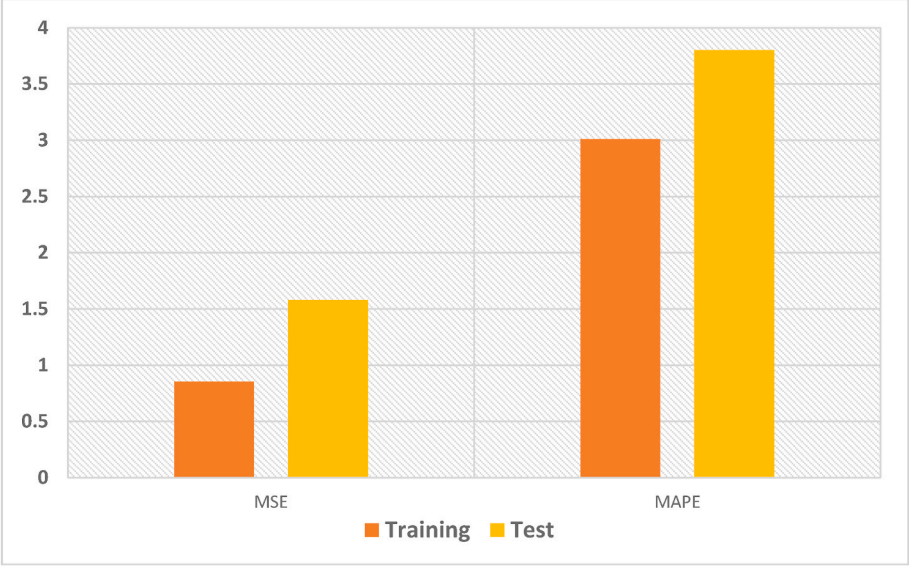


Fig. 8. MSE and MAPE results for chemical exergy of torrefied biomass in the training set and the test set.

consistent with the theoretical background. Especially, temperature appears to be a critical factor that influences the torrefied material's useful energy content. Although the influence of residence time on the output variable is positive, the characteristic is complicated in some ranges. Between 30 and 60 min, it has almost zero effect, but between 60 and 90 min, it has a significantly positive effect. The residence time demonstrate no change on the output variable between 120 min and beyond. The impact of physicochemical attributes on the output variable is more complicated than the influence of operational conditions on the output variable. Change in ash content between 2% and 7% had no influence on chemical exergy, however concentrations between 8% and beyond had a negative impact. It can be highlighted that fuels with a VM content of 65–75% and an FC content of less than 10% or more than 20% have a positive impact on the output variable. A larger dataset, on the other hand, can help to clarify these correlations. These relationships were perhaps noticed due to a lack of experimental research because certain fuels were involved in the thermolysis process under certain operational conditions. Nevertheless, it can be observed from the partial dependence plots that temperature is a strong positive parameter and ash content is a strong negative parameter.

In most of the studies, torrefaction procedure was at certain temperatures (200 °C, 250 °C, and 300 °C) and periods (30 min and 60 min), however raw biomass samples had different physicochemical characteristics. The chemical exergy of torrefied material produced under different operating conditions, even for identical raw biomass sample, is not the same since the thermolysis process converts raw material into new solid fuel. Therefore, forecasting the chemical exergy of torrefied fuel using the physicochemical properties of raw biomass requires a complex learning structure. Feature importance was extracted to better understand the effect of the features in the ANN model, as visualized in Fig. 6.

Not surprisingly, temperature is the most influential feature on chemical exergy of torrefied materials which contributes more than 30%. As mentioned above, temperature is critical in altering the physicochemical characteristic of raw biomass during torrefaction. Therefore, the chemical exergy of the solid fuel is improved due to the increment of HHV and C/O ratio. The second most effective parameter is the ash value of the raw biomass with a contribution of approximately 25%. Although ash content is quite low in biomass, it has a considerable impact on the torrefied material's chemical exergy. This may be the reason for an effect on the ratio of reactive/non-reactive structures in torrefied biomass. Then, as the third, the FC and VM content of the fuel appeared to be the effective feature on the model. Finally, the least effective parameter is time. The residence time increases the calorific value of the fuel and the C/O ratio, which increases the chemical exergy. However, many of the experiments in the dataset are for specific time periods, which might be an explanation the minor impact on ANN.

3.4. Evaluation of the ANN model

The dataset is separated into two subsets to improve the model's generalization capability: 80% for training (227 datasets) and 20% for testing (57 datasets). In the model compiling section, 20% of the training set is assigned as the validation set (45 datasets). The trial and error method was used because there is no absolute approach for determining the number for neurons in hidden layers. By minimizing the value calculated by loss function, the ANN was ran repeatedly to identify the number of neurons. The MSE converges to a minimal value as the number of epochs increased; nonetheless, at a certain number of epochs, the MSE remained constant. This indicates that the ANN's biases and weights do not change over time.

The R^2 indicates how strongly the forecasted and real values are related. It is one of the most widely used parameters to assess the model's performance. A comparison of chemical exergy of torrefied biomass is demonstrated in Fig. 7.

The presence of a few outliers within the test resulted in the R^2 score being lower than the training. Before the experimental method, the ANN can correctly predict chemical exergy for torrefied biomass. The MAPE and MSE scores for each target were also investigated. The MAPE and MSE scores for the test and training sets are shown in Fig. 8.

Fig. 8 denotes that the MSE and MAPE values for chemical exergy estimation are acceptably low. The MSE value increased in the test because the ANN's precision was poorer than in the training. When the MAPE values are compared, there is a slight difference between the two datasets, but the results of 3.009 and 3.801 are quite acceptable. These findings indicate that the ANN model is capable of accurately predicting chemical exergy of torrefied materials.

4. Conclusion

In this paper, we report the first comprehensive study using raw biomass proximate analysis results and torrefaction operating parameters to estimate the chemical exergy of torrefied biomass prior to the torrefaction process. Moreover, the model developed in this study calculates the chemical exergy directly without considering the properties of the torrefied material, such as calorific value and elemental

composition, which are required for estimating the chemical exergy of a solid fuel, as described in the methodology section. To make the developed ANN model more feasible, 284 different torrefaction operating parameters described in the literature were used to evaluate the chemical exergy of torrefied biomass. The ANN model overcomes the modeling limitations while improving the accuracy in simulating the chemical exergy of torrefied biomass prior to torrefaction in a wide range of operating conditions. Consequently, the developed machine learning approach based on ANN provides a shortcut to the complex process of torrefaction for predicting the chemical exergy of torrefied biomass.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2022.106383.

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