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EXPLORING SUSTAINABLE FUEL PRODUCTION THROUGH THERMAL BEHAVIOR ANALYSIS USING TGA AND ARTIFICIAL NEURAL NETWORK IN THE CO-PYROLYSIS OF POLYSTYRENE AND COCONUT SAWMILL RESIDUE

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ABSTRACT

This study employs Thermogravimetric Analysis (TGA) to explore co-pyrolysis potential using polystyrene (PS) and coconut sawmill residue (CSR) for liquid fuel production. Two distinct degradation stages are observed in CSR-PS blends, mirroring pure CSR samples: the initial phase (200-400°C) decomposes biomass components, while the second stage (400-550°C) targets the synthetic polymer PS within CSR-PS blends. Analyzing thermal degradation parameters reveals insights. 100% PS exhibits the highest weight loss and activation energy, highlighting PS's formidable decomposition. Conversely, 100% CSR shows the lowest weight loss and activation energy due to its organic composition. Artificial Neural Network (ANN) modeling indicates varying correlation accuracies for different blend compositions. Surprisingly, 100% PS exhibits lower correlation accuracy in predicting weight loss compared to the 80% PS blend, which achieves a perfect correlation. Conversely, 100% CSR, with simpler decomposition, has the lowest correlation accuracy. These findings illuminate the complex thermal behavior of CSR-PS blends, emphasizing the distinct degradation characteristics of PS and CSR. Implications extend to material applications and disposal strategies, emphasizing tailored approaches based on blend compositions and thermal profiles. This research advances co-pyrolysis as a sustainable avenue for liquid fuel production, providing insights for future research and practical applications.

Keywords: coconut sawmill residue, polystyrene, TGA, ANN, co-pyrolysis.

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INTRODUCTION

The increasing global population has created a growing demand for energy across various sectors heavily reliant on fossil fuels, including mechanical operations, construction, recreation, automotive, and product packaging [1]. Plastic, particularly polystyrene, has become an essential component in these industries, leading to a significant increase in plastic production and the accumulation of plastic waste [2]. Consequently, various methods for managing plastic waste have emerged, including thermochemical conversion, disposal, and recycling [8].

Projections indicate a staggering circulation of 33 billion tons of plastic between 1950 and 2050, driven by an annual increase of at least 10%. LDPE, PP, PS, and PET plastics are commonly found in municipal waste, with concerning estimates suggesting that a minimum of 8 million MT/year of plastics end up in the oceans. The Philippines is among the top 10 countries contributing to the ocean's burden of mismanaged plastic waste. Illegally disposed waste, primarily comprised of plastics, infiltrates streams and eventually contaminates seas, causing severe harm to marine life and exacerbating environmental degradation [6].

One potent strategy to diminish our reliance on fossil fuels involves the application of pyrolysis-a process integral to the thermal degradation of biomass. Pyrolysis boasts the capability of producing low-temperature chemicals from a diverse array of fuels, notably converting biomass into bio-oil. Nevertheless, the quantity and quality of bio-oil generated through conventional biomass pyrolysis have often fallen short of meeting the prerequisites for fuel applications, as indicated in numerous studies [4].

Harnessing the potential of agricultural production and processing waste such as coconut sawmill residues as an energy resource is of paramount importance, given its propensity to substantially contribute to environmental pollution if not managed judiciously. Pyrolysis oil derived from diverse biomass sources exhibits the potential for deployment as a versatile fuel. Significantly, co-pyrolysis technology, particularly when involving synthetic polymers like plastics, enhances the properties of pyrolysis oil, augmenting both its quantity and quality [14].

The domain of co-pyrolysis technology harbors immense promise, and its modeling and optimization can represent a pivotal stride in mitigating waste disposal issues [12]. Remarkably, there exists a dearth of studies exploring the co-pyrolysis of coconut sawmill residue (CSR) and polystyrene (PS) plastic.

Thermogravimetric analysis (TGA) stands as an invaluable instrument, extensively utilized to scrutinize the thermal characteristics of substances under varying heating environments. TGA facilitates the calculation of activation energy through the application of the Arrhenius equation [3].

In a parallel vein, numerous artificial neural network (ANN) models have been devised to simulate and predict co-pyrolysis characteristics [13]. While ANN

demonstrates formidable predictive prowess, it often operates akin to a "black-box" model. This research endeavors to harness the Arrhenius Law in conjunction with ANN to dissect the kinetics and thermal degradation behaviors of CSR and PS, culminating in a more holistic comprehension of the intricate interactions governing this system.

MATERIALS AND METHODS

Coconut Sawmill Residue and Polystyrene Feedstock

Waste polystyrene (PS) and coconut sawmill residue (CSR) were gathered from multiple landfill sites for the study. To prepare these feedstocks for further analysis, they underwent a series of steps. Initially, the collected feedstocks were subjected to washing to remove any impurities and contaminants. Following this, the materials were air-dried to eliminate moisture content.

To prepare for the subsequent analysis, additional processing was carried out on the feedstock. In particular, it underwent mechanical chopping or crushing, resulting in particles of approximately 1 millimeter in size to ensure the absence of temperature gradients during the process [9]. These reduced-size particles were subsequently employed in thermogravimetric analysis (TGA).

The study incorporated a wide range of combinations involving coconut sawmill residue (CSR) and polystyrene (PS) proportions. These proportions included 0%, 20%, 40%, 60%, 80%, and 100%. This diverse set of combinations was chosen to facilitate an extensive and thorough examination of the thermal degradation characteristics and behaviors exhibited by these materials across varying conditions.

Thermogravimetric Analysis of Different Samples of Coconut Sawmill Residue and Polystyrene Plastic

The analysis of the degradation behavior of coconut sawmill residue (CSR) and polystyrene (PS), as well as their various percentage proportions, was carried out using a Perkin Elmer TG (Thermogravimetric) analyzer. The analyzer had a temperature range spanning from 30°C to 900°C, and a consistent heating rate of 10°C per minute was employed. The analysis was conducted in a controlled environment with the use of nitrogen (N2) gas, which was purged at a rate of 20 ml per minute.

During each experimental run, the TGA analyzer recorded several key parameters, including:

a) Time (min): The duration of the experiment in minutes.
b) Temperature (°C): The temperature of the sample at various time points during the analysis.
c) Calculated Activation Energy (kJ/mol): This represents the energy required for specific thermal degradation processes.
d) Weight Loss (%): The percentage of weight lost by the sample as it underwent thermal degradation.

To visualize and analyze the data obtained from these experiments, the Origin Lab software was employed. This software facilitated the creation of thermal degradation charts, enabling a more in-depth examination of the degradation behavior and characteristics of CSR and PS at different percentage proportions and temperatures.

Using Values of Activation Energy

In the evaluation of activation energy and the identification of multiple degradation mechanisms, a first-order kinetic model was employed in conjunction with a synergy analysis approach [10]. Among the models used, two of them are represented by Equation 1 and Equation 2. These equations play a critical role in understanding the thermal degradation processes and mechanisms involved in the study.

$$f(x) = 1-x \quad (1)$$

$$g(x) = -\ln(1-x) \quad (2)$$

In their research, Flynn & Wall (1966) applied the Arrhenius equation, as depicted in Equation 3, to compute the kinetics of first-order processes. In this equation:

$$\frac{dx}{dt} = Ae^{\left(-\frac{Ea}{RT}\right)}(1-x) \quad (3)$$

- Ea represents the activation energy (measured in joules per mole, J mol^-1).
- A represents the collision coefficient (measured in per minute, min^-1).
- R denotes the universal gas constant (with a value of approximately 8.314 joules per mole per kelvin, J K^-1 mol^-1).

The Arrhenius equation is a frequently employed tool for explaining how reaction rates in chemical and thermal degradation processes vary with temperature. It offers valuable insights into factors such as activation energy and reaction kinetics.

Equation 4 is employed to describe the weight loss fraction (x) during a thermal degradation process. This equation relates x to the initial mass of the mixture (mi), the mass at an immediate time (mt), and the final mass (mf).

Equation 5, on the other hand, is derived from integrating Equation 2 under conditions of a constant heating rate. This equation likely provides a mathematical representation of the relationship between temperature, time, and the extent of the degradation reaction, which is valuable in characterizing the behavior of materials during thermal degradation processes.

$$x = \frac{m_t - m_i}{m_f - m_i} \quad (4)$$

$$ln\left[\frac{-ln(1-x)}{T^2}\right] = ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (5)$$

In Equation 5, the first term on the right side represents the activation energy (Ea), while the second term represents the co-pyrolysis temperature range [10]. This equation provides a mathematical relationship that combines the activation energy with temperature-related factors to characterize the behavior of a system undergoing co-pyrolysis.

To determine the activation energy, a common approach is to plot the values of $\ln(-\ln(1-x)/T^2)$ against 1/T, where:

- ln denotes the natural logarithm.
- x represents the weight loss fraction.
- T is the absolute temperature.

This graphical representation allows researchers to extract the activation energy by analyzing the slope of the resulting plot. The activation energy is a crucial parameter in understanding the kinetics of a chemical or thermal degradation process.

Artificial Neural Network Modelling

During the training of the artificial neural network (ANN), various combinations of polystyrene (PS) percentages, specifically 20%, 40%, 60%, 80%, and 100% were employed alongside a 100% coconut sawmill residue. The ANN training exclusively utilized significant thermal degradation datasets to ensure the accuracy of the model. Visual Gene Developer 2.1 was the software employed for the ANN modeling.

The neural network architecture used for all PS proportions adhered to a 3-4-4-1 topology, as illustrated in Figure-1. When designing a neural network, the challenge lies in selecting the optimal number of layers and neurons to achieve precise results. The degree of validity was employed to assess the accuracy of the artificial neural network model [11]. This architecture comprises three input nodes, four nodes in the first hidden layer, four nodes in the second hidden layer, and one output node.

In this study, specific topology settings were established for the employed artificial neural network (ANN). The ANN was configured to manage three input variables and one output variable. To enrich the complexity and learning capacity of the ANN, two hidden layers were incorporated. The initial hidden layer consisted of four nodes, and this structure was mirrored in the second hidden layer, which also featured four nodes. These configuration choices played an indispensable role in shaping the architecture and structure of the ANN.

Additionally, this study encompasses pivotal training settings for the artificial neural network (ANN). The learning rate was deliberately set at 1, and the momentum coefficient was meticulously fixed at 0.1. The Sigmoid transfer function was judiciously chosen for the ANN to optimize its performance. To maintain precision throughout the training phase, a stringent target error of 0.00001 was prescribed. The threshold initialization followed a randomized approach, akin to the random method employed for initializing the weight factors. Furthermore, the analysis update interval was thoughtfully scheduled to occur at regular intervals of 500 cycles. Collectively, these thoughtfully chosen parameters provided the framework and conditions within which the ANN underwent training and evaluation in this research context. It is imperative to underscore that these parameters hold paramount importance in ensuring the accuracy and effectiveness of the artificial neural network throughout the study.

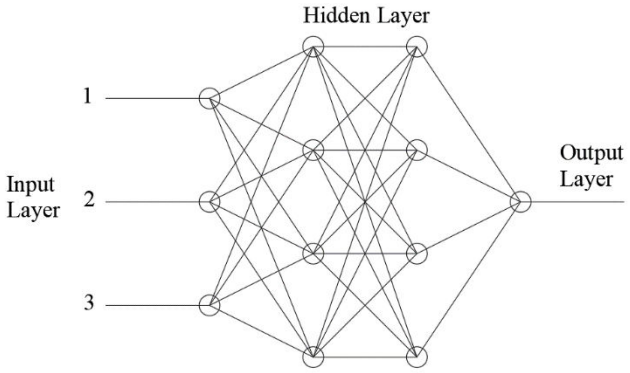

Figure-1. ANN architecture.

Before initiating the training process, the datasets underwent a crucial normalization procedure. This step was taken to ensure that the data fell within a standardized range, a practice known to enhance the efficiency of the training process.

Throughout the training process, the neural network continuously adjusted its parameters until it reached the predefined target error, which, in this case, was meticulously set at 0.00001. This target error essentially acted as a benchmark for evaluating the network's performance and guided when the training process should conclude.

In the concluding phases of the process, the predicted outputs generated by the trained neural network underwent a de-normalization step. This was executed once the network achieved the highest attainable regression coefficient. This coefficient serves as an indicator of the quality of predictions and their alignment with the actual data.

When evaluating the results of the predicted percentage weight loss against the actual percentage weight loss achieved during neural network training, a higher regression coefficient, denoted by R^2, signifies a more optimized artificial neural network architecture. A heightened R^2 value implies that the neural network has effectively acquired the necessary knowledge to make precise predictions, thus underscoring the success of the training process.

RESULTS AND DISCUSSIONS

TGA Datasets Generated

As depicted in Figure-2, the thermal degradation of CSR-PS blends exhibited a distinctive behavior occurring in two stages, specifically within temperature

ranges of 200 to 400 degrees Celsius and 400 to 550 degrees Celsius.

The peaks identified during the initial degradation stage corresponded to the breakdown of hemicellulose, cellulose, and lignin. These constituents are frequently present in biomass materials and undergo thermal decomposition within this temperature range (Im *et al*., 2022). In contrast, the peaks observed during the second degradation stage were linked to the decomposition of the PS plastic component. This stage is marked by the deterioration of the synthetic polymer.

This two-stage degradation profile provides valuable insights into the thermal behavior of CSR-PS blends, highlighting the distinct processes involved in the degradation of both biomass and plastic components within the blends. Understanding these thermal degradation stages is crucial for optimizing the utilization of such blends in various applications.

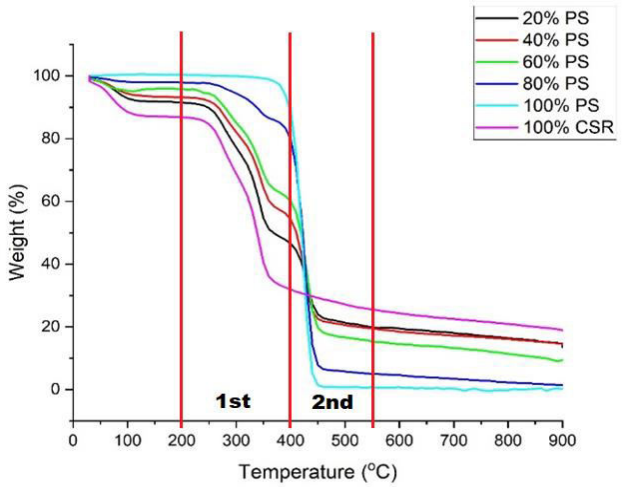

Figure-2. Coconut sawmill residue (CSR), and different CSR-PS proportions TGA curves.

Table-1 presents essential data derived from the TGA (Thermogravimetric Analysis) curves, focusing on significant thermal degradation parameters such as time, temperature, activation energy, and weight loss. Here are some key observations from the table:

a) **Highest percentage weight loss:** The highest percentage of weight loss, reaching 76.18%, was recorded under the conditions of 100% PS. This occurred at a specific time of 41 minutes and a temperature of 419.94°C. The corresponding activation energy for this degradation process was notably high, at 333.20 kJ/mol.

b) **Lowest percentage weight loss:** In contrast, the lowest percentage of weight loss, amounting to 16.73%, was recorded when dealing with 100% CSR, and this occurred within a 34-minute timeframe.

c) **Activation energy differences:** The activation energy values vary significantly between the different materials. For instance, the thermal decomposition of 100% PS yielded the highest activation energy, likely due to the specific compounds present in polystyrene. Conversely, 100% CSR exhibited the lowest activation energy at 77.20 kJ/mol, mainly attributed to its organic components.

These findings underscore the diverse thermal degradation characteristics of polystyrene (PS) and coconut sawmill residue (CSR) and provide insights into the energy requirements for their decomposition processes. Such information is valuable for understanding the behavior of these materials under varying thermal conditions and can inform their practical applications and disposal strategies.

Table-1. Thermal degradation highest results.

	Polystyrene Proportion (%)	Coconut Sawmill Residue Proportion (%)	Time (min)	Temperature (°C)	Activation Energy (kJ/mol)	Weight loss (%)
1	20	80	43	439.94	88.05	19.43
2	40	60	42	429.94	126.05	23.86
3	60	40	43	439.94	149.46	31.96
4	80	20	42	429.94	248.07	54.98
5	100	0	41	419.94	333.20	76.18
6	0	100	34	349.94	77.20	16.73

Predicted Versus Actual % Weight Loss Comparison

According to the data presented in Table-2, the highest regression coefficient was achieved with 80% PS, while the lowest coefficient was recorded for 100% CSR, standing at 99.03%. These results were obtained within a total training processing time of 10 minutes. Figures 3 through 8 depict scatter plots illustrating the relationship between predicted and actual weight loss values across various percentage proportions, all of which are based on the ANN modeling.

Table-2. Regression analysis per processing time.

	Polystyrene Proportion (%)	Coconut Sawmill Residue Proportion (%)	Regression Coefficient (R^2)	Processing Time (minutes)
1	20	80	99.1	10
2	40	60	99.78	10
3	60	40	99.16	10
4	80	20	100	10
5	100	0	99.78	10
6	0	100	99.03	10

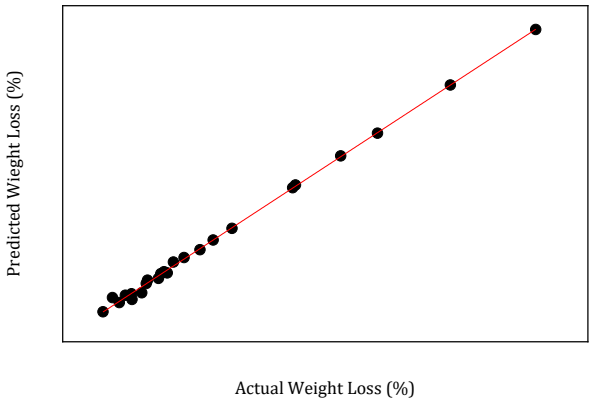

Figure-3. Predicted versus actual plots for %weight loss in 20%PS.

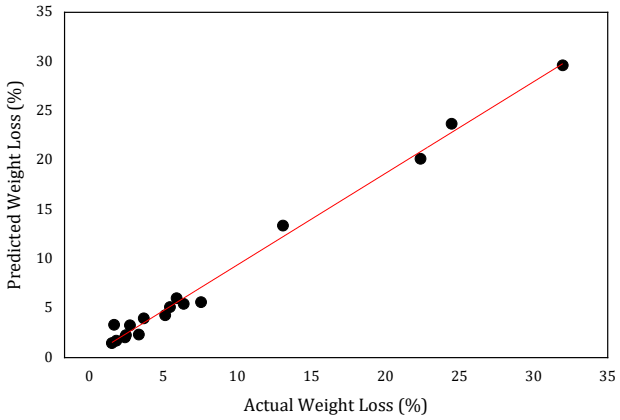

Figure-5. Predicted versus actual plots for %weight loss in 60%PS.

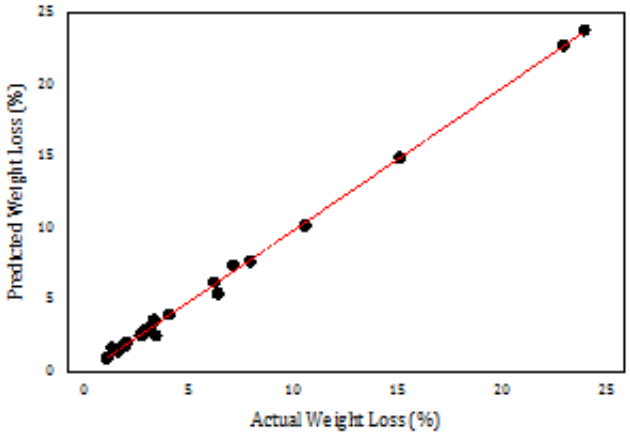

Figure-4. Predicted versus actual plots for %weight loss in 40%PS.

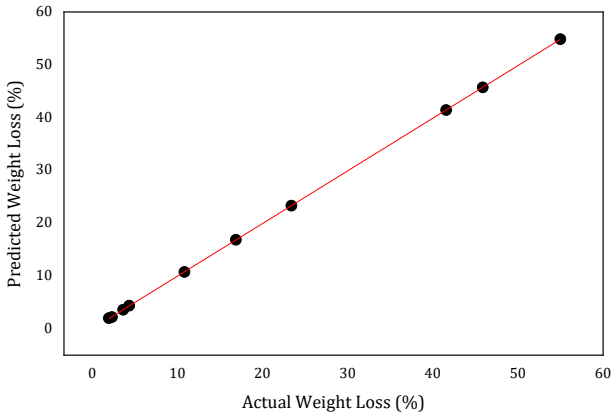

Figure-6. Predicted versus actual plots for %weight loss in 80%PS.

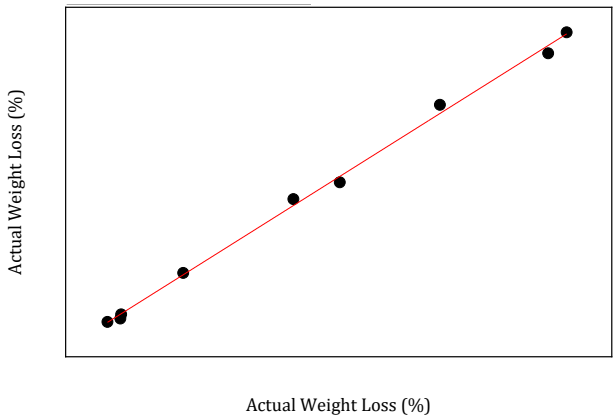

Figure-7. Predicted versus actual plots for %weight loss in 100%PS.

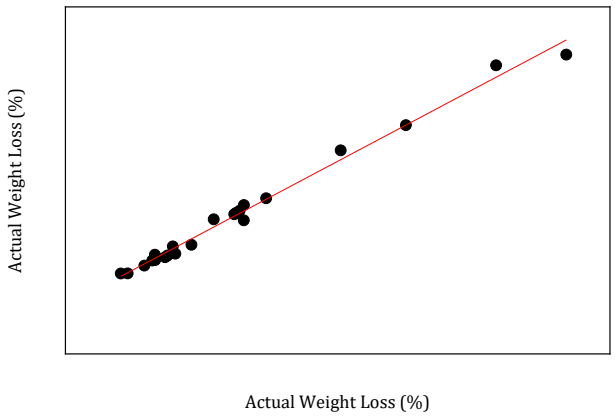

Figure-8. Predicted versus actual plots for %weight loss in 100%CSR

ARTIFICIAL NEURAL ANALYSIS

During the neural analysis of each percentage proportion, it becomes evident that we can visualize the synaptic weights associated with every neuron within each hidden layer of the neural network. Figures 9 to 14 provide a graphical representation of these weights, offering insights into network behavior. Visual Gene Developer offers an intuitive graphical interface for users to explore the trained network visually.

In this graphical representation, lines are employed to depict weight factors, while circles (nodes) represent threshold values. This visualization employs a color scheme to convey critical information:

The red color signifies a high positive number, indicating a robust positive weight factor. In contrast, the violet color denotes a high negative number, indicating a substantial negative weight factor.

The width of the lines is directly proportional to the absolute value of the weight factor or threshold value, offering a visual representation of their relative significance.

This visualization technique serves as a valuable tool for enhancing comprehension of the neural network's architecture, the strength of connections (weights), and the influence of individual neurons on the overall behavior of the network. It greatly aids in deciphering the inner workings of complex neural networks.

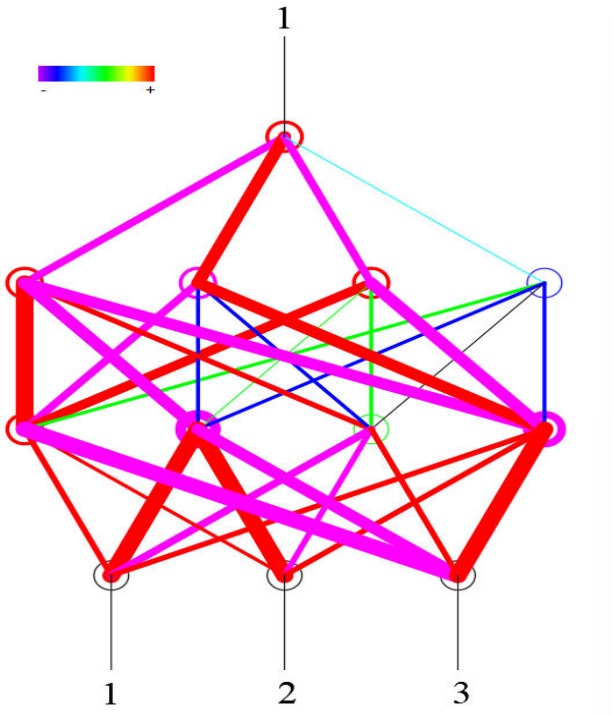

Figure-9. ANN Analysis for 20%PS.

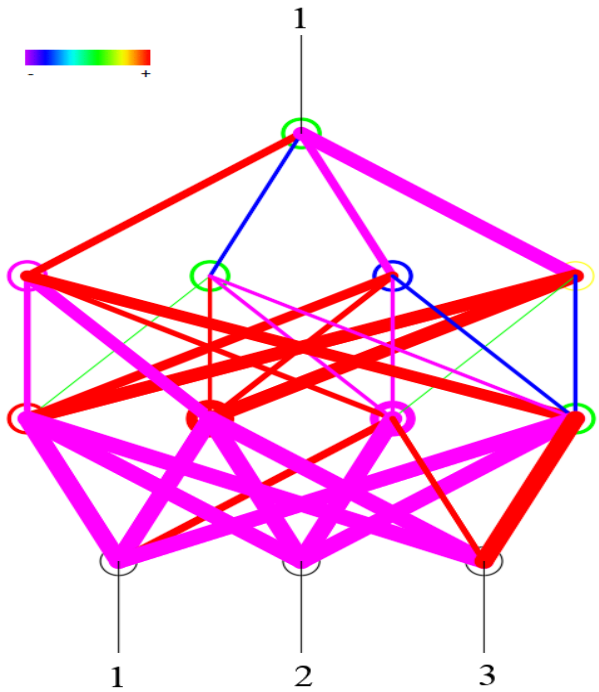

Figure-10. ANN Analysis for 40%PS.

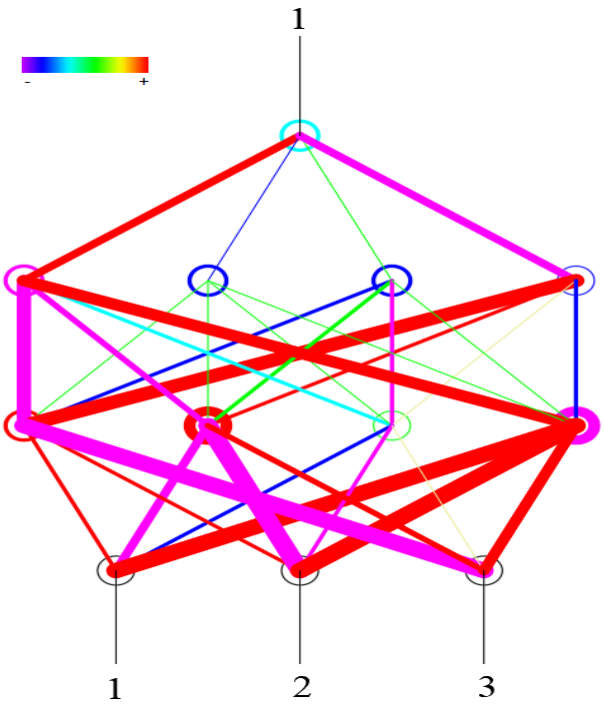

Figure-11. ANN Analysis for 60%PS.

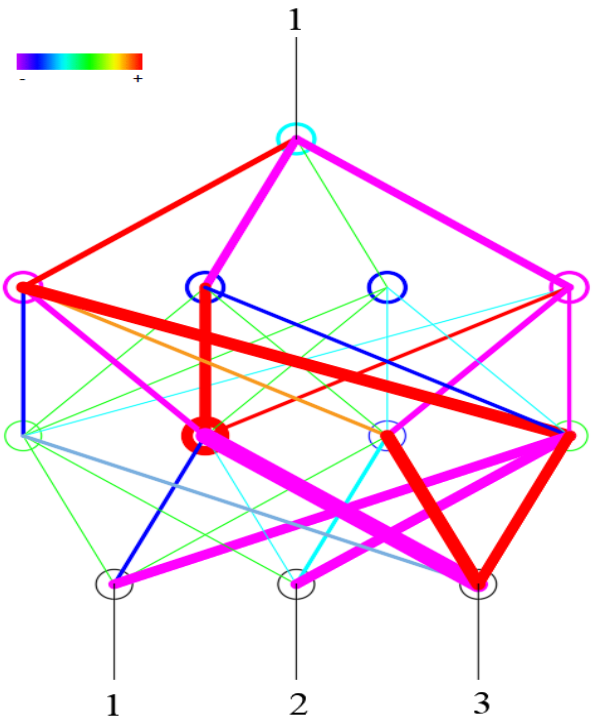

Figure-12. ANN Analysis for 80%PS.

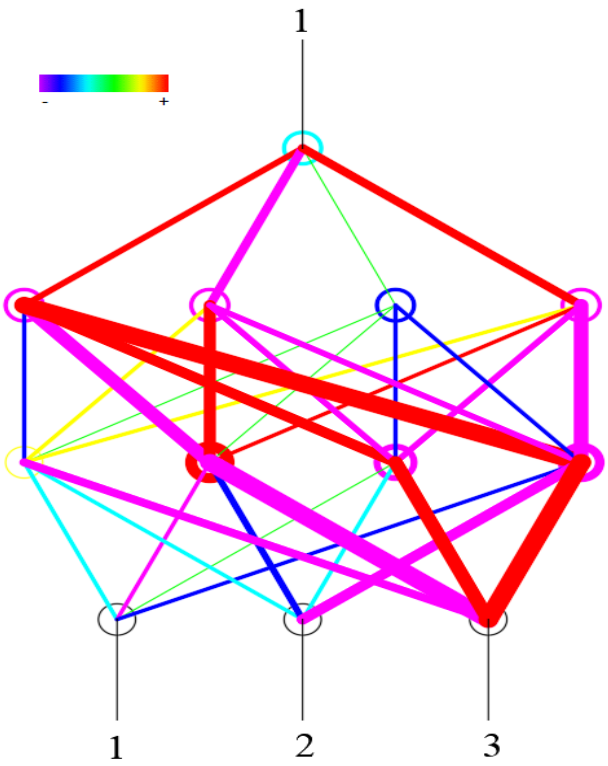

Figure-13. ANN Analysis for 100%PS.

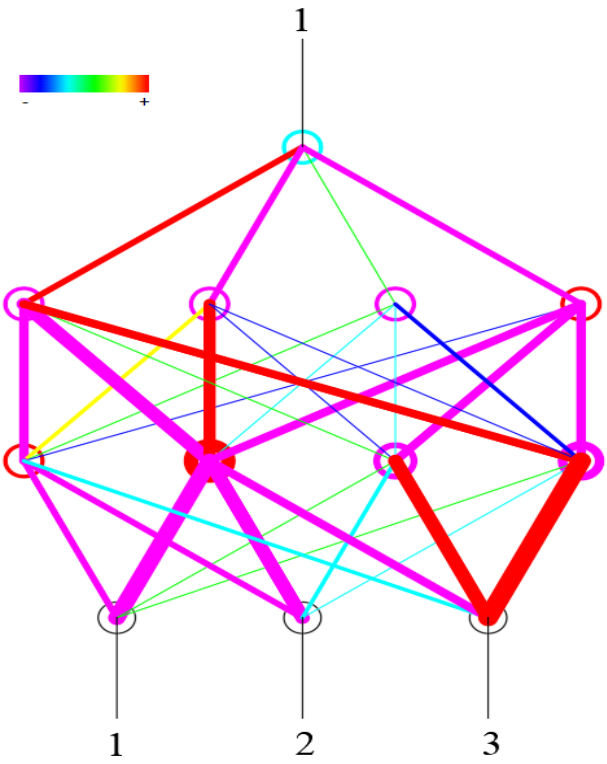

Figure-14. ANN Analysis for 100%CSR.

The outcomes generated by the neural networks are summarized in Table-4. Notably, despite 100% PS showing the highest percentage of weight loss and the highest activation energy, the results from the ANN

modeling indicate that it achieved a correlation accuracy of only 99.78%. In contrast, the configuration with 80% PS achieved a perfect correlation accuracy of 100%.

Conversely, the lowest weight loss and activation energy, which were characteristic of 100% CSR, were consistent with its position as having the lowest correlation accuracy, standing at 99.03%. These correlation accuracy values were computed after de-normalizing the predicted values obtained through simulation in the artificial neural network.

CONCLUSIONS

In conclusion, this study comprehensively investigated the thermal degradation characteristics of CSR-PS blends, uncovering a distinct two-stage degradation pattern reminiscent of that observed in 100% CSR samples. The initial stage corresponds to the decomposition of biomass constituents such as hemicellulose, cellulose, and lignin, taking place in the temperature range of 200 to 400 degrees Celsius. Conversely, the second stage entails the decomposition of the synthetic polymer, polystyrene (PS), present in the CSR-PS blends, occurring within the temperature range of 400 to 550 degrees Celsius.

- The analysis of thermal degradation parameters, including weight loss, activation energy, and time, has provided valuable insights. The highest percentage of weight loss was observed in 100% PS, with a corresponding high activation energy, highlighting the challenging nature of PS decomposition. On the other hand, 100% CSR exhibited the lowest weight loss and activation energy, reflecting its organic composition and easier thermal breakdown.
- Additionally, the Artificial Neural Network (ANN) modeling demonstrated varying correlation accuracies for different blend compositions. Surprisingly, despite 100% PS having the highest weight loss and activation energy, its correlation accuracy in predicting weight loss was lower than that of the 80% PS blend, which achieved a perfect correlation. Conversely, 100% CSR, with the lowest weight loss and activation energy, had the lowest correlation accuracy.

These findings shed light on the complex thermal behavior of CSR-PS blends and the significant differences in the degradation characteristics of PS and CSR. Such insights are invaluable for applications involving these materials and can inform disposal strategies, emphasizing the need for tailored approaches based on the specific blend compositions and their distinct thermal profiles.

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