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Machine Learning-Based Prediction of Gaseous Fuel Generation During Co-Pyrolysis of Lignin and Red Mud

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ABSTRACT

This study systematically investigated the generation behavior of gaseous fuels (e.g., H₂, CO, and CH₄) during the pyrolysis of waste materials (lignin and red mud) and developed machine learning (ML)-based models for accurate prediction of gas yields. Pyrolysis experiments were carried out under varying reaction atmospheres (i.e., N₂, CO₂, and N₂/CO₂) and waste material mixing ratios to comprehensively evaluate the gas generation characteristics. Pearson correlation analysis identified reaction temperature and gas flow rate as the most influential parameters governing gas yields. Three ML models—artificial neural network (ANN), XGBoost (XGB), and Extra Trees (ET)—were developed to compare the gas generation prediction performances. The ANN model achieved superior accuracy, with coefficients of determination of $R^2 = 0.992$ (H₂), 0.989 (CH₄), and 0.994 (CO). SHapley Additive exPlanations (SHAP) analysis was subsequently applied to quantify the relative contribution of each input variable to model predictions. Building on the ANN model, two-dimensional (2D) simulations were performed to explore the combined effects of temperature, gas flow rate, and red mud content on gas generation. Simulation results revealed consistent increases in H₂, CO, and CH₄ yields under specific combinations of these conditions. Maximum predicted yields of H₂ (>3.5 mol%), CH₄ (>1.2 mol%), and CO (>7.0 mol%) were identified under their respective optimal conditions. These findings demonstrate that ML-based approaches offer a robust and interpretable framework for predicting gas generation behavior and optimizing process conditions in pyrolysis systems.

1 | Introduction

CO₂-assisted pyrolysis has recently emerged as a promising thermochemical conversion strategy for biomass valorization, attracting considerable attention due to its dual functionality in enhancing gas production and enabling simultaneous CO₂ utilization [1, 2]. Unlike conventional inert atmospheres (e.g., N₂), the use of CO₂ as a reaction medium introduces additional reaction pathways, most notably the Boudouard reaction ($C + CO_2 \rightarrow 2CO$) and dry reforming ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$), which can substantially alter the gas-phase composition and overall product

distribution [3]. These CO₂-involved reactions not only promote the formation of syngas components (H₂ and CO) but also offer a promising pathway for carbon-neutral or carbon-negative process design. Pyrolysis is a well-established thermochemical process that decomposes biomass into gaseous, liquid, and solid products under oxygen-free or oxygen-limited conditions [4]. Among these products, light gaseous fuels (H₂, CO, and CH₄) are of particular importance as key constituents of syngas, with broad applications in downstream energy conversion and chemical synthesis [5]. Lignin, a major component of lignocellulosic

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biomass, possesses a highly cross-linked aromatic network composed of guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units [6, 7]. During pyrolysis, lignin undergoes a series of competing reactions including ether bond cleavage, aromatic ring fragmentation, radical formation, and recombination resulting in complex and highly nonlinear reaction pathways [8]. The inherent complexity of these multistep processes makes it practically challenging to predict and control gas generation behavior with conventional approaches [9, 10].

Beyond intrinsic precursor characteristics, inorganic constituents play a critical role in governing pyrolysis reactions [11, 12]. Metal oxides and mineral phases can catalyze hydrocarbon cracking, tar reforming, and redox processes, thereby facilitating the conversion of heavy intermediates into light gaseous fuels such as H_2 and CO [13, 14]. In this context, the utilization of industrial by-products as sources of catalytic metal oxides has attracted growing interest, providing both improved process efficiency and sustainable waste valorization. Among such materials, red mud, a bulk by-product of the Bayer process for alumina refining, is particularly noteworthy owing to its rich composition of catalytically active metal oxides (e.g., Fe_2O_3 , Al_2O_3 , and TiO_2) [15]. Notably, Fe-based species can promote the cracking and transformation of volatile intermediates and facilitate carbon- CO_2 gasification reactions, thereby enhancing the generation of syngas components such as H_2 and CO under pyrolytic conditions. For example, Yang et al. [16] reported that red mud-derived catalysts significantly enhanced gaseous fuel production during biomass-plastic co-pyrolysis, with H_2 and CO yields increasing by more than eight and six times, respectively, owing to enhanced reforming and gas-phase conversion reactions. Similarly, de Souza et al. [17] demonstrated that red mud enhanced syngas production and exhibited pronounced tar-cracking activity during biomass thermochemical conversion while simultaneously improving bio-oil quality through the decomposition of oxygenated compounds and primary pyrolysis products. These findings suggest that red mud holds considerable potential for tuning the reaction behavior in CO_2 -assisted pyrolysis systems. Despite these promising attributes, CO_2 -assisted pyrolysis inherently involves a highly complex reaction network governed by multiple interdependent variables, including feedstock composition, inorganic content, reaction temperature, and gas atmosphere. The strong coupling and nonlinear interactions among these variables substantially hinder mechanistic interpretation and limit the identification of optimal operating conditions through conventional experimental approaches [18–21]. In particular, systematic studies investigating the synergistic effects of lignin-based feedstocks and waste-derived inorganic catalysts under varying reaction atmospheres (N_2 vs. CO_2) remain insufficiently investigated.

To address these limitations, machine learning (ML)-based data-driven approaches have recently gained considerable prominence as powerful tools for modeling complex thermochemical systems [22, 23]. Recent studies have increasingly employed ML approaches to predict gaseous fuel production from thermochemical conversion processes. For example, ML models have been successfully applied to biomass-plastic co-pyrolysis and biomass pyrolysis systems for predicting gas and syngas yields while simultaneously identifying key governing variables through explainable AI approaches [24, 25]. More recently, hybrid ML frameworks have also demonstrated promising performance for syngas property prediction from lignocellulosic biomass conversion processes

[26]. However, ML-based prediction of gaseous fuel generation in biomass-industrial waste co-pyrolysis systems remains largely unexplored. ML algorithms are capable of capturing nonlinear relationships and high-dimensional interactions that are difficult to describe using traditional kinetic or empirical models. In particular, tree-based ensemble methods such as XGBoost (XGB) and Extra Trees (ET) are well-studied for modeling complex variable interactions and quantifying feature importance, while artificial neural networks (ANNs) demonstrate superior capability in approximating highly nonlinear reaction behaviors [27]. Furthermore, interpretability frameworks such as SHapley Additive exPlanations (SHAP) enable quantitative assessment of variable contributions, providing mechanistic insights that extend beyond black-box predictions [28].

In this study, the pyrolysis of red mud-lignin mixtures was systematically investigated under both N_2 and CO_2 atmospheres to elucidate gas generation behavior, with particular focus on H_2 , CH_4 , and CO yields. Based on the experimental dataset, multiple ML models, including ANN, XGB, and ET, were developed to predict gas yields and comparatively evaluate their predictive performance. SHAP analysis was subsequently employed to identify the key governing variables and quantify their respective contributions to gas formation. To further enhance process-level understanding, two-dimensional (2D) response surface simulations were conducted using the best-performing trained models to visualize gas yield landscapes as functions of temperature and gas flow rate.

2 | Materials and Methods

2.1 | Sample Preparation and Thermogravimetric Analysis (TGA)

Red mud was obtained from the Korea Institute of Geoscience and Mineral Resources (KIGAM) (Republic of Korea), and alkali lignin (kraft lignin; Sigma-Aldrich, USA) was used as the biomass feedstock. Prior to experimentation, both materials were dried at $80^\circ C$ for 24 h and used for TGA and pyrolysis experiments. Three sample compositions were prepared to systematically investigate the effect of red mud content on lignin thermal degradation: (i) pure lignin, (ii) red mud-lignin (0.5:1, w/w), and (iii) red mud-lignin (2:1, w/w). Each sample was weighed at the specified mass ratios and thoroughly homogenized using a mortar and pestle. TGA was conducted using a thermogravimetric analyzer (STA449 F5 Jupiter, NETZSCH, Germany). For single-stock experiments, approximately 10 mg of pure lignin was used, whereas red mud-lignin mixtures were prepared at mass ratios of 0.5:1 and 2:1 (w/w). All samples were heated from 40 to $900^\circ C$ at a constant heating rate of $10^\circ C\ min^{-1}$ under N_2 , CO_2 , or a mixed gas atmosphere ($N_2/CO_2 = 1:1$, v/v). The total gas flow rate was maintained at $100\ mL\ min^{-1}$ using an internal mass flow controller (MFC).

2.2 | Pyrolysis Process Setup

Pyrolysis experiments were performed in a batch-type tubular furnace reactor (FT-830, DAIHAN Scientific, Republic of Korea). A photograph of the pyrolysis unit and a schematic illustration of the experimental setup are provided in Figure S1. Samples were placed in two alumina crucibles, each containing 1 g of lignin

with varying red mud content (red mud:lignin = 0:1, 0.5:1, and 2:1, w/w). The crucibles were positioned at the center of a quartz tube (inner diameter: 2.4 cm and length: 60 cm). Both ends of the tube were sealed with stainless-steel Ultra-Torr fittings (SS-16-UT-6) equipped with reducing unions (SS-1610-6-4, Swagelok, USA) to ensure a controlled gas flow. Prior to heating, the reactor was thoroughly purged with the selected reaction gas. Ultra-high purity ($\geq 99.9\%$) N_2 and CO_2 gases were supplied by Green Gas Co. (Republic of Korea). Experiments were conducted under N_2 , CO_2 , or a mixed gas ($N_2/CO_2 = 1:1$, v/v) at a flow rate of 200 mL min^{-1} , regulated by MFC (Brooks Instruments 5950 series E, USA). Based on the heated reactor volume ($\sim 136 \text{ mL}$, 30 cm heating zone) and gas flow rate, the gas residence time was approximately 41 s. All samples were heated from 100 to 700°C at a constant heating rate of $10^\circ\text{C min}^{-1}$. Gaseous products were analyzed using a micro gas chromatography (Micro-GC, Fusion, INFICON, Switzerland). The concentrations of H_2 , CH_4 , and CO were monitored at 3 min intervals, with calibration performed using a certified standard gas mixture (N_2 balance; RIGAS, Republic of Korea).

2.3 | Dataset Preparation for Modeling

In this study, an experimental dataset was constructed to predict the concentrations of gaseous fuels (e.g., H_2 , CH_4 , and CO) generated during pyrolysis. The input variables comprised reaction temperature ($100\text{--}700^\circ\text{C}$), red mud content ($0\text{--}4 \text{ g}$), N_2 gas flow rate ($0\text{--}200 \text{ mL min}^{-1}$), and CO_2 gas flow rate ($0\text{--}200 \text{ mL min}^{-1}$), while the output variables were defined as the concentrations of the produced gases (e.g., H_2 , CH_4 , and CO). The ranges and types of all variables are summarized in Table 1. These variables were selected because they represent the key factors influencing the gas generation behavior during the pyrolysis process. In particular, reaction temperature is widely recognized as the most influential operating parameter affecting pyrolysis pathways and product distribution, while feedstock composition and reaction atmosphere (i.e., N_2 and CO_2 flow rates) strongly influence catalytic activity, gasification reactions, and gaseous product formation [21, 29]. All input variables were treated as continuous numerical features for model training. To evaluate the generalization performance of the developed models, the dataset was partitioned into training and test sets at a ratio of 8:2. The complete dataset consisted of 147 data points, of which 118 data points (80%) were allocated to the training dataset and the remaining 29 data points (20%) were reserved for the testing

dataset. Prior to model training, all input variables were normalized to minimize the influence of scale differences among variables and to enhance the stability and convergence of the training process.

2.4 | Model Architecture and ML Model Evaluation

Python-based ML algorithms were employed to predict the concentrations of gaseous fuels generated during pyrolysis. Three models ANN, XGB, and ET were developed and their predictive performances were systematically compared. The ANN model, built upon a multilayer neural network architecture, is particularly effective in capturing complex nonlinear relationships among input variables by learning hierarchical feature representations through successive hidden layers [27]. In contrast, XGB and ET are decision tree-based ensemble models that repeatedly partition the feature space based on input variables, offering high predictive accuracy and robust generalization performance [30]. Specifically, XGB and ET were selected as representative models of boosting and bagging methods, respectively, to enable a systematic comparison of the two principal ensemble learning approaches [31, 32].

The entire dataset was partitioned into training and test sets at a 8:2 ratio. The hyperparameters of all models were optimized using the Bayesian optimization method. Bayesian optimization, a representative sequential model-based optimization (SMBO) technique, was employed to efficiently determine the optimal hyperparameters of each model [33]. This approach utilizes a probabilistic surrogate model to estimate the objective function and iteratively selects promising search points by balancing exploration and exploitation. Owing to its ability to identify optimal solutions with a limited number of evaluations, Bayesian optimization is widely used for ML hyperparameter tuning and process optimization [34, 35]. For the ANN model, key hyperparameters, including the activation functions, number of nodes per hidden layer, batch size, and learning rate, were systematically optimized, and the Adam optimizer was employed to update weights and biases during training. For the XGB model, optimized hyperparameters included the number of trees, maximum tree depth, learning rate, data sampling ratio, and L1 and L2 regularization parameters (reg_alpha and reg_lambda). For the ET model, the number of trees, maximum tree depth, minimum number of samples, and maximum feature ratio were optimized. The predictive performance of all models was evaluated using three matrices: the coefficient of determination (R^2), mean absolute error (MAE), and mean squared error (MSE), the definitions of which are provided in Equations (1)–(3). R^2 quantifies the proportion of variance in the observed data explained by the model, with values closer to 1 indicating superior predictive performance. MAE represents the average absolute deviation between predicted and actual values, while MSE penalizes larger errors more heavily by averaging the squared residuals. In general, a well-performing model is characterized by R^2 approaching 1 and MAE and MSE approaching 0.

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}, \quad (1)$$

$$MSE = \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}, \quad (2)$$

TABLE 1 | Types and ranges (minimum and maximum values) of variables used for modeling.

Parameters	Variable type	Minimum	Maximum
Temperature	Input variable	100	700
Red mud	Input variable	0	4
N_2 gas (flow rate)	Input variable	0	200
CO_2 gas (flow rate)	Input variable	0	200
H_2	Output variable	0	3.670238
CH_4	Output variable	0	1.682417
CO	Output variable	0	10.33279

$$\text{MAE} = \frac{1}{n} \sum_{i=1}^n |y_i - \hat{y}_i|, \quad (3)$$

where n is the total number of data points, y_i is the actual output data, $\hat{y}_i$ is the output data predicted by the trained model, and $\bar{y}$ is the mean of all the observed output data.

2.5 | SHAP Analysis

SHAP analysis was conducted to elucidate the relationships between input variables and gas generation during pyrolysis. SHAP is a game theory-based interpretability framework that quantitatively assesses the contribution of each input variable to model predictions and has been widely adopted to interpret complex interactions among process variables in ML models [36]. In thermochemical conversion research, SHAP has been successfully applied to compare the performance of various ML models and to interpret nonlinear relationships between key operating parameters [37]. In the present study, SHAP analysis was therefore employed as an effective diagnostic tool for identifying and ranking the influence of critical operating variables on pyrolysis gas generation. The SHAP value is calculated as described in Equation (4) [38].

$$\phi_i(x) = \sum_{S \subseteq F \setminus \{i\}} \frac{|S|!(|F| - |S| - 1)!}{|F|!} \left[f_{S \cup \{i\}}(x_{S \cup \{i\}}) - f_S(x_S) \right], \quad (4)$$

where $\phi(x)$ denotes the SHAP value for variable i , F denotes the full set of variables, S denotes the subset of F excluding variable i , f_s denotes the model built using only the variables in S , and x_s denotes the corresponding values of those variables.

3 | Results and Discussion

3.1 | Thermolytic Behaviors of Red Mud–Lignin Mixtures

TGA was performed to investigate the thermal degradation behavior of pure lignin and red mud–lignin mixtures (Figure 1). As shown in Figure 1a, the TG profile of lignin under a N_2 atmosphere exhibited one prominent weight loss stage below 500°C , with a final residual mass of 42.7% at 900°C . A gradual mass loss observed above 500°C can be attributed to the progressive carbonization of the lignin-derived char [39]. In the corresponding DTG profile, a minor peak below 125°C corresponds to the evaporation of moisture, while the principal peak at 378°C represents the maximum devolatilization rate associated with the thermal cleavage of ether bonds and aromatic structures within the lignic matrix [40]. In comparison, the TG profile of lignin under a CO_2 atmosphere followed a mass loss pattern similar to that observed under N_2 up to 746°C (Figure 1b). Beyond this temperature; however, a pronounced mass loss occurred, resulting in a markedly lower final residual mass of 5.6%. Correspondingly, an additional peak emerging above 746°C in the DTG profile, which was not observed under N_2 , is attributed to the onset of the Boudouard reaction, whereby CO_2 promotes the gasification of solid carbon residue to yield CO at elevated temperatures [41].

Compared to pure lignin (Figure 1a), the addition of red mud yielded a higher final residual mass (54.3%) under a N_2 atmosphere (Figure 1c), reflecting the contribution of inorganic components to the solid residue. In the corresponding DTG profile, the principal peak position remained nearly unchanged, whereas the peak intensity was notably reduced. This reduction is primarily attributed to the dilution effect of inorganic components on the overall volatile content of the mixture. Furthermore, an additional peak emerged at 771°C that was absent in the pure lignin sample, which is likely associated with phase transformations of inorganic components (e.g., iron minerals) in red mud, potentially influencing high-temperature reaction pathways [42]. Under a CO_2 atmosphere (Figure 1d), the red mud–lignin mixture exhibited a higher residual mass (30.8%) relative to pure lignin, consistent with the trend observed under N_2 . In the corresponding DTG profile, the Boudouard reaction peak, observed at 746°C for pure lignin, shifted to a lower temperature of 666°C in the presence of red mud and simultaneously split into two distinct features. This behavior suggests that red mud actively influences the Boudouard reaction, likely by lowering activation energy through catalytic interactions between metal oxide phases and carbon residues at elevated temperatures [43].

At a higher red mud loading (2:1), the influence of inorganic components became increasingly pronounced under a N_2 atmosphere (Figure 1e). The final residual mass increased from 54.3% (0.5:1) to 68.6%, reflecting the greater proportion of inorganic material in the mixture. This trend suggests that the residue yield was primarily governed by the increasing fraction of nonvolatile mineral phases present in the red mud. In the corresponding DTG profile, the principal peak position remained nearly unchanged; however, the reduction in peak intensity indicates progressively suppressed lignin devolatilization with increasing red mud content [44]. Furthermore, the additional peak associated with inorganic phase transformations shifted from 771°C (0.5:1) to 786°C (2:1), suggesting that higher red mud loading elevates the temperature at which inorganic transformations occur. Under a CO_2 atmosphere (Figure 1f), the final residual mass increased systematically with red mud loading, rising from 30.8% (0.5:1) to 60.3% (2:1). In the corresponding DTG profile, the Boudouard reaction peak in the red mud–lignin (2:1) mixture occurred at a temperature comparable to that observed for the red mud–lignin (0.5:1) mixture; however, the peak profile became more distinctively resolved into multiple features. This observation suggests that increasing red mud loading progressively intensifies the influence on high-temperature carbon- CO_2 interactions, likely attributable to the greater availability of catalytically active metal oxide phases.

Under a mixed N_2/CO_2 (1:1) atmosphere, the thermal behavior of the red mud–lignin (0.5:1) mixture closely resembled that observed under CO_2 (Figure 1g). The TG profile exhibited a markedly lower final residual mass compared to that under N_2 , approaching the value obtained under CO_2 . In the corresponding DTG profile, a pronounced Boudouard reaction peak emerged at a temperature comparable to that observed under CO_2 , suggesting that even a partial CO_2 concentration is sufficient to dominate the high-temperature reaction behavior [45]. It should be noted; however, that TGA primarily captures solid-phase and gas–solid interactions and does not account for homogeneous gas-phase reactions. Therefore, the observed trends should be interpreted as indicative of overall reaction tendencies rather

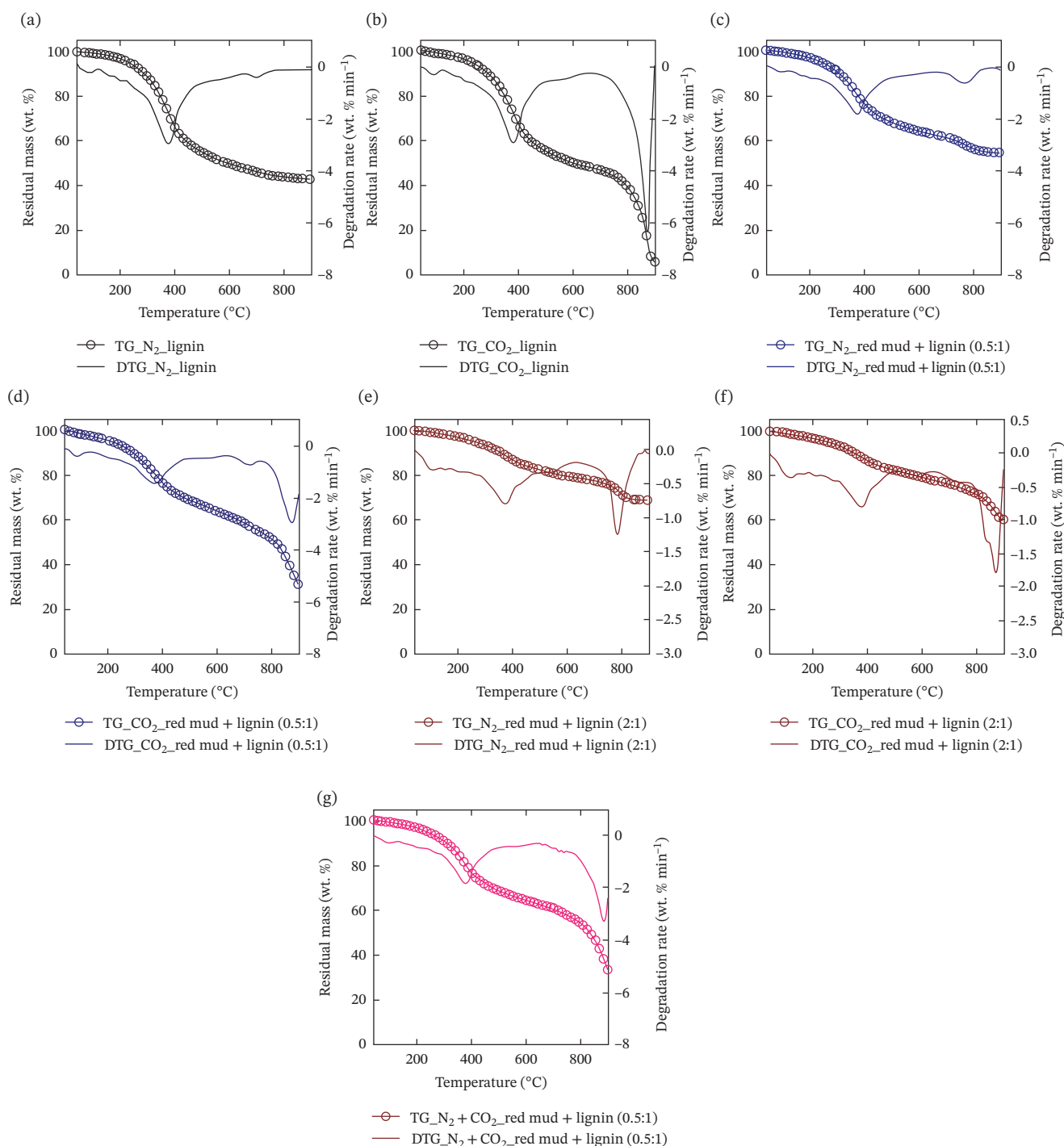


FIGURE 1 | TG and DTG profiles of lignin and red mud–lignin mixtures with different mixing ratios during pyrolysis under N_2 and CO_2 atmospheres: (a, b) lignin, (c, d) red mud–lignin (0.5:1), (e, f) red mud–lignin (2:1), and (g) red mud–lignin (0.5:1) under a mixed N_2/CO_2 atmosphere.

than a comprehensive representation of the underlying pyrolysis chemistry.

3.2 | Gas Evolution Behavior During Pyrolysis

The temperature-dependent evolution of gaseous fuels during pyrolysis is presented in Figure 2. Overall, gas evolution behavior varied significantly with the reaction atmosphere and red mud loading, particularly for H_2 and CO . As shown in Figure 2a, H_2 evolution from pure lignin increased above $400^\circ C$, reaching a maximum at approximately $670^\circ C$. At elevated temperatures

($\geq 580^\circ C$), the H_2 concentration under N_2 was substantially higher than that under CO_2 , likely due to the involvement of CO_2 in secondary reactions that consume H_2 [39]. The addition of red mud shifted the onset of H_2 formation to a lower temperature ($\sim 310^\circ C$), suggesting that red mud promotes H_2 -generating reactions in the low-temperature region, possibly through the catalytic activity of metal oxide components [46]. Under a N_2 atmosphere, the red mud–lignin (0.5:1) mixture yielded the highest H_2 concentration, whereas further increasing the red mud loading to a 2:1 ratio resulted in a notable decrease. In contrast, under a CO_2 atmosphere, higher red mud loading progressively

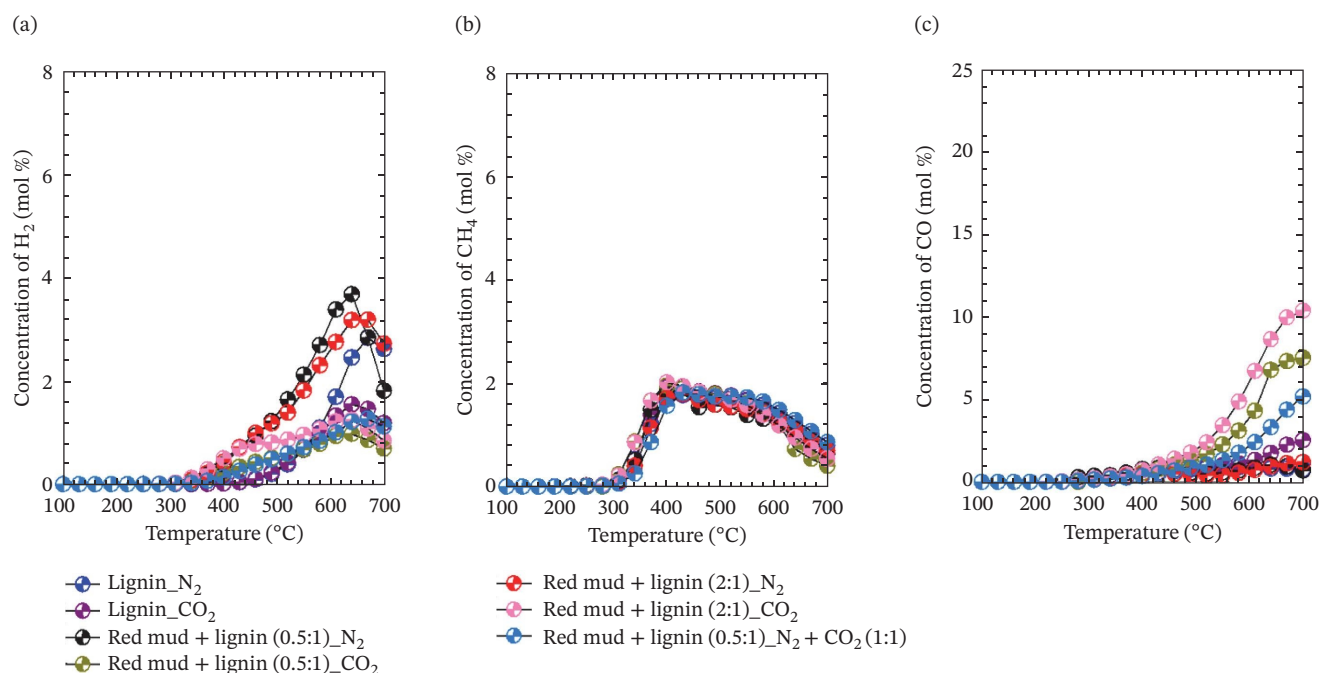


FIGURE 2 | Evolution of gaseous fuels during pyrolysis of lignin and red mud–lignin mixtures under different atmospheric conditions: (a) H_2 , (b) CH_4 , and (c) CO concentrations as a function of temperature for lignin and red mud–lignin mixtures with mass ratios of 0.5:1 and 2:1 under N_2 , CO_2 , and N_2/CO_2 (1:1) atmospheres.

enhanced H_2 formation across most of the temperature range, although the overall H_2 concentration remained lower than that under N_2 at high temperatures ($\geq 430^\circ C$). Under the mixed-gas condition ($N_2/CO_2 = 1:1$), the H_2 evolution profile followed a trend similar to that observed under CO_2 at an intermediate concentration level.

As shown in Figure 2b, CH_4 evolution from pure lignin commenced above $310^\circ C$, reaching a maximum at approximately $430^\circ C$. Unlike H_2 and CO , the CH_4 evolution profiles exhibited minimal variation with the reaction atmosphere and red mud loading, with both peak position and intensity remaining largely unchanged across all conditions. This insensitivity suggests that CH_4 formation is primarily governed by the primary devolatilization of lignin rather than secondary gas-phase or gas–solid reactions [47]. As shown in Figure 2c, CO evolution from pure lignin followed similar trends under both N_2 and CO_2 atmospheres up to $550^\circ C$. Above this temperature, a marked increase in the CO concentration was observed under CO_2 , whereas the CO concentration under N_2 declined, resulting in substantially higher CO yields under CO_2 at $700^\circ C$. This divergence indicates that CO formation at elevated temperatures is predominantly driven by CO_2 -involved gas–solid reactions, most notably by the Boudourd reaction [48]. The addition of red mud progressively enhanced CO formation under CO_2 , with CO concentration increasing with red mud loading. Accordingly, the highest CO concentration was observed for the red mud–lignin (2:1) mixture. This suggests that red mud actively facilitates CO -generating reactions, likely through catalytic interactions between metal oxide phases and carbon residues at elevated temperatures [29]. Under the mixed gas condition ($N_2/CO_2 = 1:1$), the CO profile followed a trend similar to that observed under pure CO_2 , although the CO concentration was lower. This indicates that even partial CO_2 availability can influence CO formation, while the overall extent of the reaction remains dependent on the CO_2 concentration.

The overall gas distribution under varying reaction conditions is presented in Figure S2. Under a N_2 atmosphere, H_2 accounted for the dominant fraction of the total gaseous fuels, whereas CO became the predominant species under a CO_2 atmosphere. The addition of red mud further enhanced CO production under CO_2 , with the effect becoming more pronounced at higher red mud loadings. In contrast, the relative contribution of CH_4 remained nearly constant across all experimental conditions. Collectively, these results confirm that the overall gas distribution is primarily governed by the reaction atmosphere, while red mud predominantly influences the absolute extent of gas production rather than the relative distribution pattern among gaseous fuels. Specifically, H_2 production was favored under a N_2 atmosphere at a red mud/lignin ratio of 0.5:1, whereas CO production was maximized under a CO_2 atmosphere with a higher red mud content (red mud/lignin = 2:1). These observations suggest that red mud primarily acts as a catalytic promoter that enhances the overall gas production, while the reaction atmosphere determines the final gas composition.

3.3 | Statistical Distributions and Correlations of Process Variables and Gas Products

Figure 3 presents the statistical distributions and inter-variable correlations of the experimental datasets used to model gas yields during the pyrolysis of pure lignin and red mud–lignin mixtures. The violin plots in Figure 3a illustrate the distributional characteristics of both process variables and gaseous fuel concentrations, providing insight into the variability and range of the experimental space explored. Notably, reaction temperature exhibits the widest distribution among all input variables, reflecting the broad operating window systematically investigated to capture the thermochemical response of the system. Among the product gases, H_2 and CO show comparatively broader

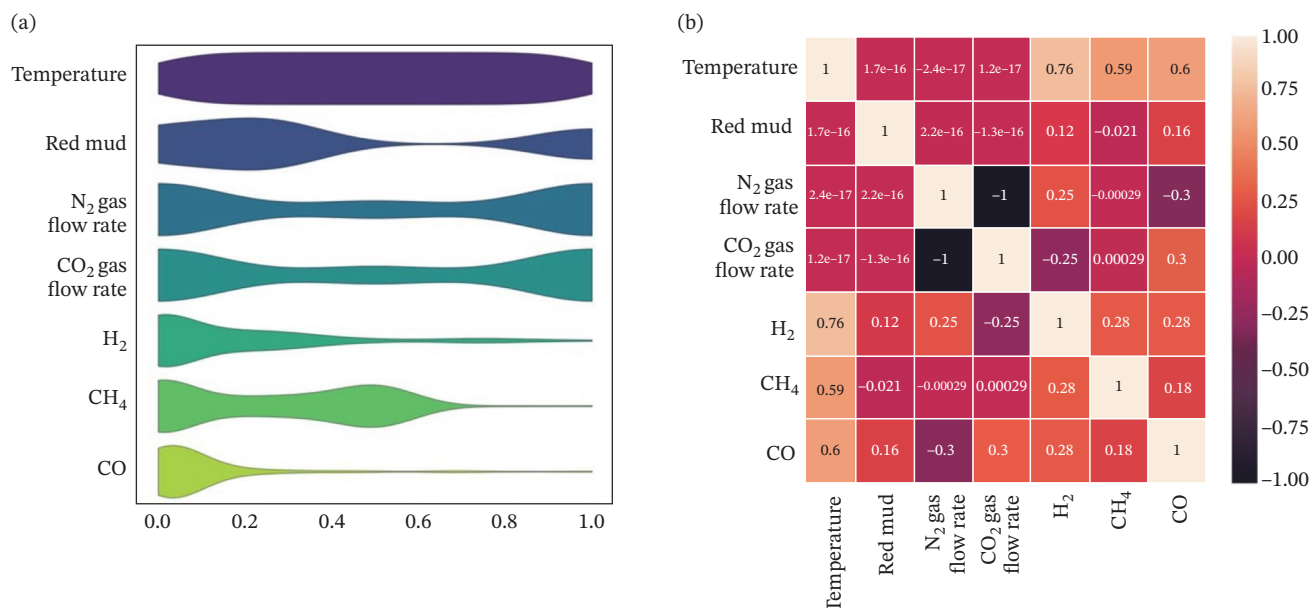


FIGURE 3 | Statistical analysis of experimental variables used for gas production during lignin and red mud co-pyrolysis. (a) Distribution of normalized process variables and product gases represented by violin plots. (b) Pearson correlation matrix of process variables and gas products (H₂, CH₄, and CO).

distributions than CH₄, suggesting that their formation is more sensitive to variations in operating conditions, whereas CH₄ is generated within a relatively narrower concentration regime.

The Pearson correlation matrix presented in Figure 3b reveals that reaction temperature exhibits strong positive correlations with H₂ ($r=0.76$), CO ($r=0.60$), and CH₄ ($r=0.59$), confirming that gas yields are predominantly governed by thermal effects during pyrolysis. The N₂ and CO₂ gas flow rates display a perfect inverse correlation ($r=-1$), reflecting the experimental design in which their relative proportions were systematically varied. The CO₂ gas flow rate shows a weak positive correlation with the CO yield ($r=0.30$) and a weak negative correlation with H₂ ($r=-0.25$), indicating that CO₂ participates in carbon gasification reactions, thereby promoting CO formation while moderately suppressing H₂ generation. Conversely, the N₂ gas flow rate exhibits a negative correlation with CO ($r=-0.30$) and a weak positive correlation with H₂ ($r=0.25$), suggesting that an inert atmosphere suppresses CO₂-driven gasification pathways and reduces the availability of reactive species [49]. The red mud mixing ratio shows only weak correlations with all gaseous fuels (H₂: $r=0.12$, CH₄: $r=-0.021$, and CO: $r=0.16$), indicating that its direct linear influence on gas yields is limited relative to

reaction temperature and gas atmosphere. Nonetheless, given the experimentally observed variations in gas generation with red mud loading, this discrepancy suggests that red mud–lignin interactions likely involve nonlinear synergistic effects that are not adequately captured by linear correlation analysis.

3.4 | ML Framework for Gas Prediction

Figure 4 presents the overall workflow of the ML-based framework developed for gas yield prediction in this study. This framework comprises four sequential stages: model selection, data preparation, model training and optimization, and post-processing. In the model selection stage, three ML algorithms, XGB, ET, and ANN, were employed to predict the gas yield during pyrolysis. These algorithms were selected for their demonstrated capability to capture complex nonlinear relationships and high-dimensional interactions among process variables, making them well-suited for modeling the interdependencies between pyrolysis operating conditions and gas generation behavior. Among them, XGB represents the boosting-based tree ensemble family, whereas ET adopts the bagging-based ensemble approach, thereby enabling a systematic comparative evaluation of two fundamentally distinct tree-based learning strategies.

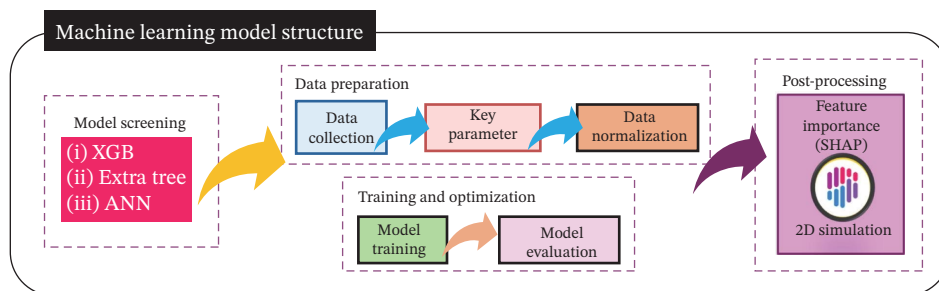


FIGURE 4 | Workflow of the machine learning framework used in this study: model selection, data preparation, model training and optimization, and post-processing.

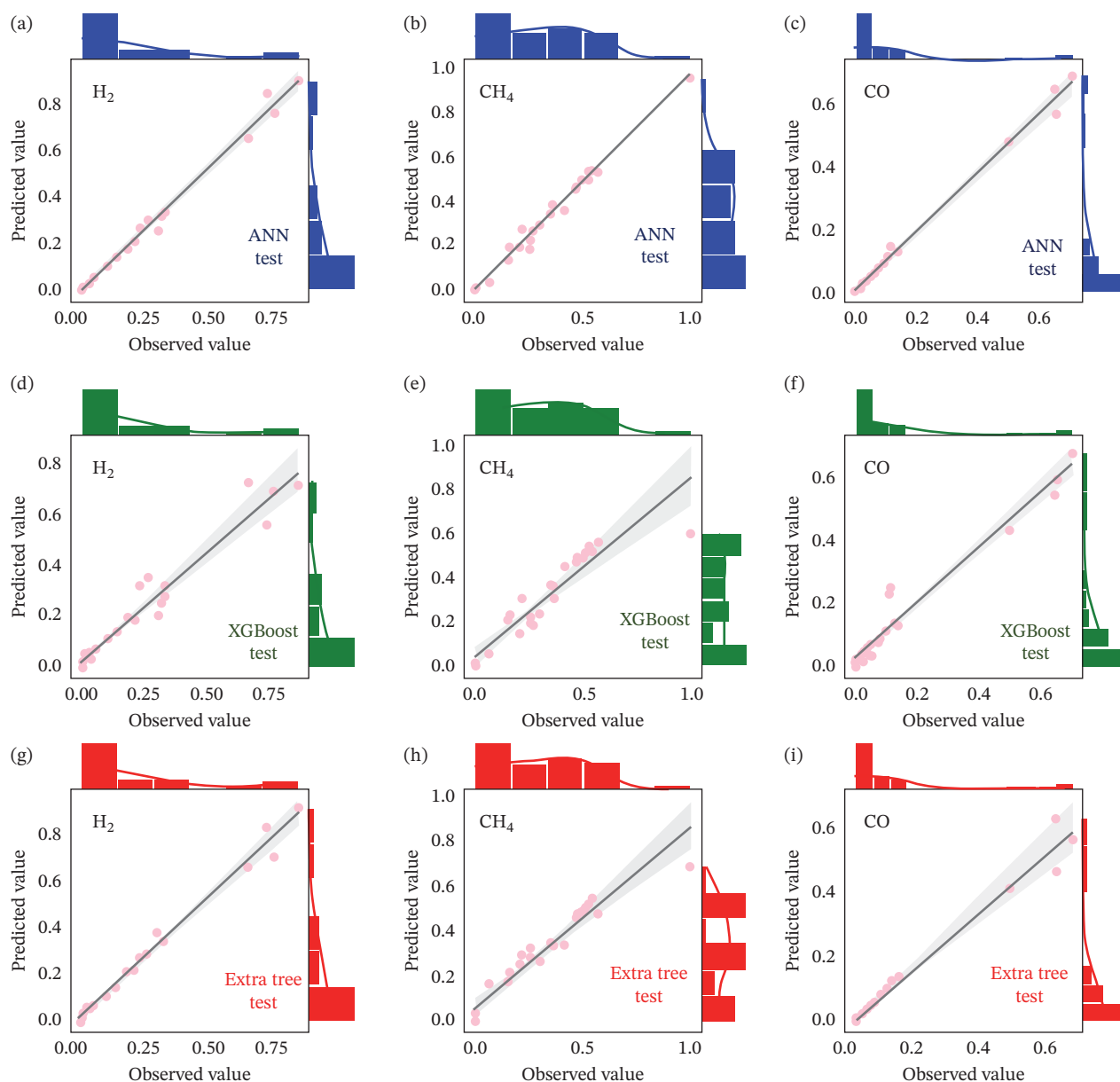


FIGURE 5 | Predicted versus observed values of H_2 , CH_4 , and CO for the test dataset using ANN (a–c), XGB (d–f), and ET (g–i) models.

In the data preparation stage, experimental process variables and gaseous fuel data were organized into a structured dataset suitable for ML model training. The input variables comprised reaction temperature, lignin content, red mud content, N_2 gas flow rate, and CO_2 gas flow rate, while the output variables were defined as the concentrations of gaseous fuels (H_2 , CH_4 , and CO). All input variables were subsequently normalized to enhance training stability and minimize the influence of scale discrepancies among the variables. In the model training and optimization stage, each model was trained on the normalized dataset and rigorously evaluated for predictive performance. Model validation was conducted using both training and test datasets, and predictive performance was assessed based on R^2 and RMSE. In the final post-processing stage, SHAP analysis was applied to interpret the predictions for the trained models, quantitatively assessing the relative contribution and importance of each input variable to the gas yield prediction. Additionally, 2D response surface simulations were performed using the best-performing trained model

to visualize the distribution of gas yield as a function of temperature and the gas flow rate ratio (N_2/CO_2).

3.5 | Evaluation of ML Models for Gas Production Prediction

Figure 5 presents the parity plots comparing predicted and experimentally measured concentrations of H_2 , CH_4 , and CO generated during the pyrolysis of pure lignin and red mud–lignin mixtures, as obtained from the ANN, XGB, and ET models. The hyperparameters of each model were optimized using the Bayesian optimization, and the optimized values are summarized in Table S1–S3. The training results of all three models are provided in the Supporting Information (Figures S3–S5). As shown in Figure 5a–c, the ANN model demonstrates excellent agreement between predicted and measured values, with data points closely and uniformly distributed along the parity line across the full concentration range. The high predictive accuracy achieved

for all gas species (H_2 : $R^2=0.993$, CH_4 : $R^2=0.990$, and CO : $R^2=0.994$) confirms that the ANN model effectively captures the intrinsic nonlinear relationships governing gas formation during pyrolysis. This performance indicates that the pyrolysis process is dominated by complex interactions among reaction temperature, gas atmosphere, and feedstock composition, which are inherently difficult to represent using conventional linear or rule-based modeling approaches [50]. Furthermore, the strong generalization performance observed on the test dataset implies that the model has learned physically meaningful process relationships rather than merely memorizing the training data.

In contrast, the XGB model (Figure 5d–f) achieves a moderate level of predictive accuracy; however, systematic deviations from the parity line are evident when compared with the ANN model. These deviations are particularly pronounced in CH_4 prediction ($R^2=0.889$), while relatively higher accuracy is maintained for H_2 ($R^2=0.957$) and CO ($R^2=0.961$), albeit with localized prediction errors in certain concentration ranges. These results indicate that although tree-based ensemble models are capable of capturing interactions among process variables, they exhibit inherent limitations in accurately representing complex and continuous nonlinear reaction behaviors under varying process conditions. This limitation is more evident for CH_4 formation, which is governed by secondary cracking and recombination reactions that are particularly difficult to discretize within a tree-based partitioning framework. Similarly, the ET model (Figure 5g–i) reproduces the overall trends of the experimental dataset; however, it exhibits clear limitations in predictive accuracy and stability relative to the ANN model. While relatively high accuracy is achieved for H_2 ($R^2=0.990$) and CO ($R^2=0.980$), the predictive performance for CH_4 deteriorates notably ($R^2=0.929$), accompanied by increased prediction errors across the concentration range. In particular, the enlarged deviations observed in the high-concentration region suggest that tree-based models encounter structural difficulties in capturing nonlinear behaviors in sparsely populated regions of the feature space, which inherently restricts their capacity to represent smooth and continuous reaction characteristics across the full operating range.

A comparative evaluation of the three models demonstrates that the ANN model provides the most accurate and consistent predictions across all gaseous fuels, with particularly superior performance for H_2 and CH_4 . This suggests that the formation of these gases is governed by strongly coupled nonlinear interactions, including competing reaction pathways and synergistic effects between lignin and red mud components. The superior predictive performance of the ANN model can be attributed to its multilayer neural network architecture, which enables effective approximation of high-dimensional nonlinear relationships among input variables. In contrast, the prediction performance for CO is comparably consistent across all three models, indicating that CO formation follows relatively well-defined and thermochemically predictable reaction pathways. This behavior is likely associated with dominant thermochemical reactions, such as carbon gasification and decarbonylation, which exhibit monotonic and consistent trends with respect to the reaction temperature and gas atmosphere [50]. Furthermore, analysis of the residual distributions confirms that all three models successfully reproduce the overall statistical characteristics of the experimental dataset. However, only the ANN model maintains high predictive accuracy

consistently across the entire operating range, effectively capturing both universal thermochemical trends and localized nonlinear variations in gas generation behavior.

3.6 | Gas Production Mechanisms Based on SHAP Analysis

As shown in Figure 6a, SHAP analysis for H_2 prediction clearly identifies the reaction temperature as the most dominant input variable. SHAP values increase markedly at elevated temperatures, confirming that the H_2 yield is strongly enhanced with increasing temperature. The CO_2 gas flow rate is also an influential variable, exhibiting a positive contribution under higher CO_2 conditions. This behavior suggests that CO_2 actively participates in carbon gasification reactions at elevated temperatures, thereby promoting H_2 formation pathways. In contrast, red mud and N_2 gas flow rate exert comparatively minor contributions to the H_2 prediction. As shown in Figure 6b, reaction temperature remains the most influential variable for CH_4 production; however, the overall SHAP value distribution is notably narrower compared to those of H_2 and CO , reflecting a relatively weaker dependence on CH_4 formation. Both CO_2 and N_2 gas flow rates exhibit mixed positive and negative SHAP contributions, implying that CH_4

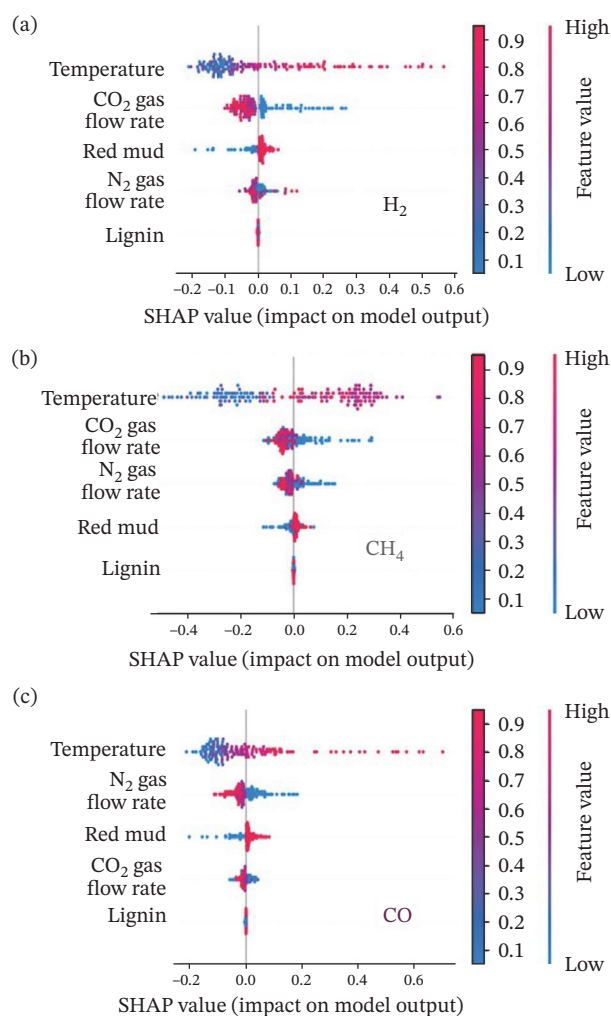


FIGURE 6 | SHAP summary plots illustrating the feature importance and impact of input variables on model predictions for (a) H_2 , (b) CH_4 , and (c) CO using the ANN model.

formation is governed by competing reaction pathways rather than a single dominant thermochemical mechanism. Notably, the contribution of red mud content is minimal, suggesting that CH_4 formation is primarily controlled by the intrinsic thermal decomposition behavior of lignin rather than catalytic interactions with inorganic phases [51].

As shown in Figure 6c, CO yield is also strongly dependent on reaction temperature, with SHAP values increasing substantially under high-temperature conditions, confirming that CO formation is predominantly driven by thermal activation. The N_2 gas flow rate exhibits a negative SHAP contribution in certain regions, indicating a dilution effect that suppresses CO-generating gasification reactions. Meanwhile, the CO_2 gas flow rate demonstrates a partially positive contribution, attributable to CO_2 -involved gasification reactions that actively generate CO. Red mud content shows a small yet discernible contribution, suggesting that metal oxide components partially facilitate CO production through catalytic interactions [16].

It is important to note that although lignin content was included as an input variable, it exhibits relatively low importance in SHAP analysis. This is attributed to the fact that the lignin content was held constant across all experimental conditions, resulting in negligible variability as an input feature. Since SHAP values quantify the contribution of variable changes to the model output, the influence of lignin is inherently underrepresented. Nonetheless, lignin serves as the primary carbon source consistently across all experimental conditions, and its limited representation in the SHAP results reflect the absence of variation rather than a lack of mechanistic significance. In contrast, red mud does not function as an independent gas-generating source but rather as a catalytic promoter that enhances the pyrolysis and gasification of lignin-derived intermediates. Its metal oxide

constituents (e.g., Fe_2O_3 and Al_2O_3) are known to facilitate carbon bond cleavage, structural rearrangement, and gasification reactions, collectively contributing to improved gas yield [52]. However, the catalytic influence of red mud is partly masked by dominant contributions of reaction temperature and gas atmosphere, resulting in its comparatively moderate representation in SHAP analysis. Collectively, these findings indicate that gas generation behavior is primarily governed by reaction temperature and gas atmosphere, while lignin serves as the principal carbon source and red mud functions as a secondary catalytic promoter. Importantly, the SHAP-based interpretation is consistent with the established pyrolysis reaction mechanisms, demonstrating that the developed ML framework not only achieves high predictive accuracy but also effectively captures the physicochemical interactions among key process variables.

3.7 | 2D Simulation Analysis of Gaseous Fuels Formation

Figure 7 presents the 2D response surface simulation results obtained from the trained ANN model, illustrating the predicted concentrations of H_2 , CH_4 , and CO as functions of reaction temperature and two key process variables, the gas flow rate ratio (N_2/CO_2) and red mud content. The lignin-to-red mud ratio was fixed at 1:1 for all simulations. This approach enables comprehensive and quantitative visualization of the gas generation behavior across a wide range of operating conditions. The combined effects of reaction temperature and gas flow rate ratio are presented in Figure 7a–c. As shown in Figure 7a, the H_2 concentration remains relatively low below 500°C but increases sharply at elevated temperatures, particularly above 600°C . This trend reflects the enhanced contribution of secondary gasification and reforming reactions under high-temperature conditions.

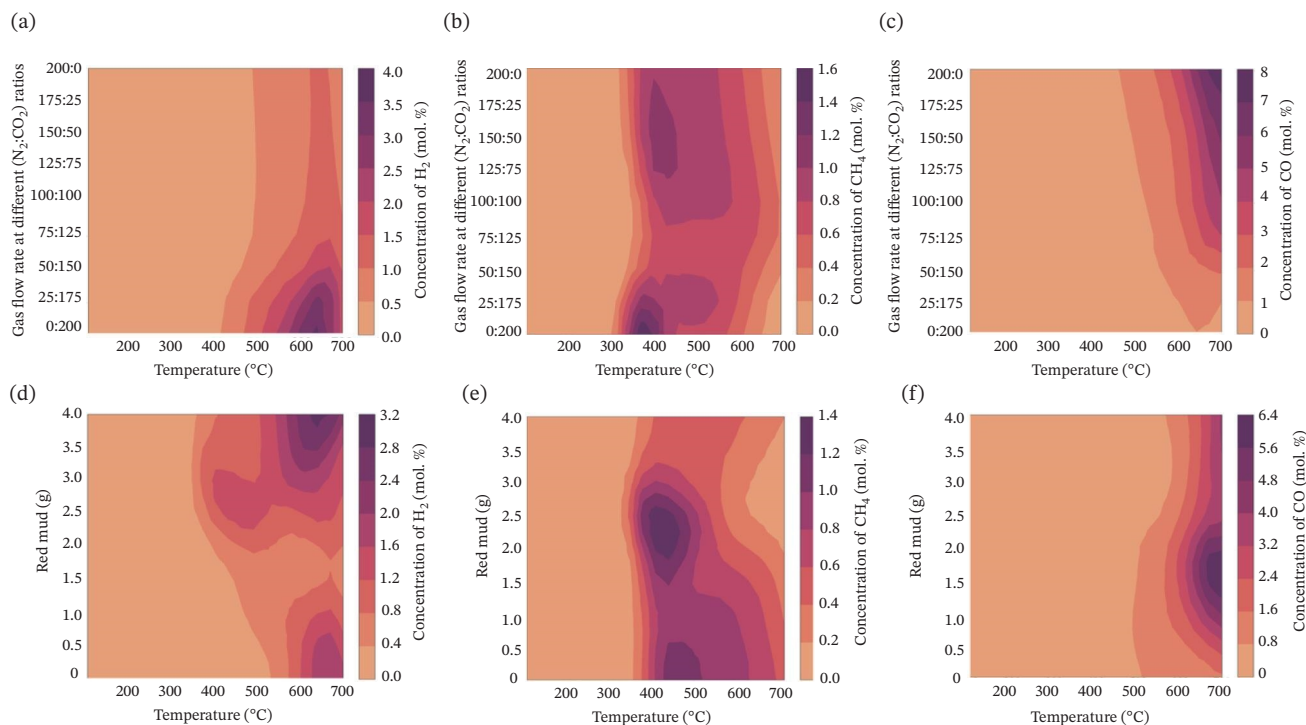


FIGURE 7 | 2D simulation results showing predicted gas concentrations versus temperature and gas flow rate ratio (N_2/CO_2). (a) H_2 , (b) CH_4 , (c) CO; and versus red mud content: (d) H_2 , (e) CH_4 , (f) CO.

Furthermore, H_2 production is progressively promoted under higher N_2 flow ratios, suggesting that an inert atmosphere facilitates thermal cracking and carbon conversion pathways, likely by suppressing competitive CO_2 -driven reactions such as dry reforming and the reverse water-gas shift reaction. As shown in Figure 7b, the CH_4 concentration distribution exhibits a distinct maximum within the intermediate temperature range (350–500°C), followed by a gradual decline at higher temperatures. This behavior is consistent with the primary generation of CH_4 during the initial devolatilization stage of lignin pyrolysis, while the subsequent decline at elevated temperatures is attributable to the consumption of CH_4 via secondary cracking and reforming reactions, resulting in progressively decreasing CH_4 concentrations [53].

As shown in Figure 7c, the CO concentration increases substantially with temperature, particularly above 600°C, a trend strongly associated with the onset of thermally activated carbon gasification reactions [54]. Furthermore, higher CO_2 flow ratios enhance CO formation, confirming that CO_2 actively participates in gasification reactions, most notably the Boudouard reaction, thereby promoting CO generation under CO_2 -rich atmospheres [55, 56]. Figure 7d–f illustrates the combined effects of reaction temperature and red mud loading on gas yields. As shown in Figure 7d, H_2 yields increase with both reaction temperature and red mud content, with the effect of red mud being particularly pronounced at elevated temperatures. This indicates that metal oxide constituents in red mud play a catalytic role in enhancing carbon conversion and gasification reactions, thereby facilitating H_2 formation [57]. Similarly, as shown in Figure 7e, CH_4 formation is favored at intermediate temperatures and moderate red mud loadings, whereas excessive red mud content or further temperature increases result in declining CH_4 concentrations, attributable to intensified catalytic cracking and reforming reactions. Figure 7f shows that the CO yield is substantially enhanced under high-temperature conditions combined with moderate to high red mud loadings. This behavior suggests that red mud-derived metal oxides effectively catalyze carbon- CO_2 interactions and facilitate gasification pathways, contributing to increased CO generation [58].

4 | Conclusion

In this study, the generation behavior of major gases (H_2 , CH_4 , and CO) during the individual pyrolysis of pure lignin and co-pyrolysis of a red mud–lignin mixtures was systematically investigated, and a ML-based predictive framework was developed for gas yield prediction. TGA revealed that the primary thermal decomposition of lignin occurs within the temperature range of approximately 300–450°C and that the pyrolysis behavior is significantly modified in the presence of red mud. In particular, under a CO_2 atmosphere, an additional mass loss was observed in the high-temperature region above approximately 700°C, indicating the activation of gasification reactions such as the Boudouard reaction and secondary reforming reactions. This behavior confirms that metal oxide constituents present in red mud function as catalytic sites that promote carbon gasification reactions at elevated temperatures. To predict gas yields, ANN, XGB, and ET models were developed based on experimental datasets comprising reaction temperature, lignin and red mud

mixing ratio, and N_2 and CO_2 gas flow rates as input variables. Comparative evaluation of model performance demonstrated that the ANN model achieved the highest predictive accuracy for all gaseous fuels (H_2 : $R^2 = 0.992$, $MSE = 0.0006$, $MAE = 0.0112$, CH_4 : $R^2 = 0.989$, $MSE = 0.0006$, $MAE = 0.0017$, CO : $R^2 = 0.994$, $MSE = 0.0003$, $MAE = 0.0079$), outperforming better than the XGB (H_2 : $R^2 = 0.956$, $MSE = 0.003$, CH_4 : $R^2 = 0.889$, $MSE = 0.0067$, $MAE = 0.0394$, CO : $R^2 = 0.961$, $MSE = 0.0017$, $MAE = 0.0241$) and ET (H_2 : $R^2 = 0.990$, $MSE = 0.0008$, $MAE = 0.0165$, CH_4 : $R^2 = 0.929$, $MSE = 0.0049$, $MAE = 0.0370$, CO : $R^2 = 0.979$, $MSE = 0.0020$, $MAE = 0.0174$). These results confirm that the ANN model effectively captures the complex nonlinear relationship between pyrolysis process variables and the gas generation behavior.

SHAP-based variable importance analysis further revealed that reaction temperature is the most dominant factor governing the generation of all gaseous fuels, followed by CO_2 and N_2 gas flow rates as secondary yet significant contributors. These results confirm that the gas generation behavior is primarily governed by reaction temperature and gas atmosphere, which together determine the selectivity and extent of gas formation during pyrolysis and gasification. Furthermore, 2D response surface simulations based on the trained ANN model demonstrate that gas yield distributions are highly sensitive to variations in reaction temperature and the gas flow rate ratio (N_2/CO_2). In particular, an optimal operating region was identified in which H_2 and CO yields increase markedly at elevated temperatures above 600°C, whereas CH_4 formation is favored within the intermediate temperature range of approximately 350–500°C. Overall, this study provides a ML-based predictive framework capable of accurately predicting and interpreting gas generation behavior during the pyrolysis and co-pyrolysis of biomass feedstocks and industrial by-products, offering practically valuable insights for the design and optimization of waste-to-energy and CO_2 utilization systems.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Supporting Information.** The supporting information material includes the photograph of the pyrolysis unit and schematic illustration of the experimental setup (Figure S1). The Gas composition (H₂, CH₄, and CO) distribution under different feed ratios and gas atmospheres (Figure S2). Concentrations of (a) H₂, (b) CH₄, and (c) for the trained ANN model using the training dataset (Figure S3). The concentrations of (a) H₂, (b) CH₄, and (c) CO for the trained XGB model using the training dataset (Figure S4). The concentrations of (a) H₂, (b) CH₄, and (c) CO for the trained ET model using the training dataset (Figure S5). Bayesian optimization results of the ANN model for gas production prediction in co-pyrolysis (Table S1). Bayesian optimization results of the XGB model for gas production prediction in co-pyrolysis (Table S2). Bayesian optimization results of the ET model for gas production prediction in co-pyrolysis (Table S3).