



Optimization of Tobacco-Stem Bio-Oil Production by Catalytic Pyrolysis Using Activated Natural Zeolite and Response Surface Methodology

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ABSTRACT

Tobacco stem is a lignocellulosic agricultural residue with potential for bio-oil production through catalytic pyrolysis. This study investigated the effects of pyrolysis temperature, reaction time, and acid-activated natural zeolite loading using Response Surface Methodology (RSM) with a Box–Behnken Design. Bio-oil yield, density, viscosity, and pH were evaluated, supported by FTIR and GC-MS characterization. The distilled bio-oil yield ranged from 15.47 to 68.79 wt%, with the highest yield obtained at 550°C, 3 h, and 10 wt% zeolite. The RSM model for bio-oil yield was statistically significant ($p=0.0474$), with zeolite loading being the most influential factor ($p=0.0121$). In contrast, the models for density, viscosity, and pH were not statistically significant. Numerical optimization identified a model-predicted candidate condition of 527.70°C, 2.55 h, and 12.36 wt% zeolite, with a predicted distilled bio-oil yield of 69.08 wt%. Experimental validation is required to assess the predictive accuracy of this condition. The results indicate that activated natural-zeolite loading was the most influential statistically significant factor affecting bio-oil yield within the investigated domain.

Keywords: bio-oil, catalytic pyrolysis, natural zeolite, response surface methodology, tobacco stem.

1. INTRODUCTION

The increasing generation of agricultural residues has stimulated the development of thermochemical technologies for converting biomass into renewable fuels and value-added chemicals. Among these technologies, pyrolysis is particularly attractive because lignocellulosic biomass can be thermally converted under oxygen-limited conditions into condensable liquids, solid char, and non-condensable gases. The product distribution and properties are strongly affected by feedstock composition, temperature, residence time, heating rate, reactor configuration, and secondary vapor reactions. In particular, cellulose, hemicellulose, and lignin undergo different primary decomposition pathways and generate a complex mixture of oxygenated compounds, phenolics, acids, furans, ketones, and other products. Consequently, controlling the interaction between

feedstock characteristics and process conditions is essential for improving both bio-oil yield and quality [1–4].

Tobacco stem is an important but comparatively underutilized lignocellulosic agricultural residue. In addition to its lignocellulosic components, tobacco biomass contains nitrogen-containing constituents that may influence the composition of its pyrolysis products. Previous studies have demonstrated the feasibility of converting tobacco residues into bio-oil through pyrolysis. Khuenkaeo et al. reported a maximum bio-oil yield of approximately 55 wt% from tobacco processing waste using an ablative reactor under vacuum at 600°C, while the resulting oil contained alkanes, aromatic compounds, and nitrogen-containing compounds [4]. More specifically, Ma et al. reported that the highest bio-oil yield from waste tobacco stem during slow pyrolysis occurred at

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approximately 600°C and identified nitrogen transformation as an important feature of the conversion process [5]. These findings demonstrate that tobacco stem has substantial potential as a pyrolysis feedstock, but its characteristic nitrogen chemistry and complex product composition must be considered when developing routes for bio-oil production.

The complexity of tobacco-stem pyrolysis also creates challenges in obtaining bio-oil with desirable chemical and physicochemical characteristics. Tobacco-derived bio-oil can contain oxygenated and nitrogen-containing compounds that influence acidity, stability, calorific value, and potential downstream utilization. Recent studies have therefore explored strategies for controlling the composition of tobacco-stem pyrolysis products. For example, co-pyrolysis of waste tobacco stem with corn stalk was reported to substantially reduce nitrogen-containing compounds in the resulting bio-oil, demonstrating the importance of controlling reaction pathways and feedstock interactions [6]. Other recent studies have focused on selective catalytic conversion using metal-supported biochar, hierarchical HZSM-5, and dual ZIF-67/ZSM-5 catalysts to enhance the formation of phenolics, hydrocarbons, or nitrogen-containing products [7–10]. These developments highlight the importance of integrating catalyst properties and process conditions when controlling the yield and composition of catalytic pyrolysis products [8–10].

Among heterogeneous catalysts, zeolites are particularly attractive for catalytic pyrolysis because their acidity, pore structure, porosity, and shape selectivity can promote cracking, dehydration, decarbonylation, decarboxylation, deoxygenation, and aromatization of biomass-derived oxygenates. The catalytic performance of zeolites is closely associated with the accessibility of active sites and the interaction between pore structure and catalyst acidity. Liang et al. emphasized that acidity and porosity are among the key

zeolite characteristics governing the transformation pathways of biomass-derived vapors, while Mishra et al. highlighted the relationship between zeolite structure, pore characteristics, acidity, and the production of aromatic and deoxygenated products [11–13].

Although synthetic zeolites such as HZSM-5 generally provide well-defined catalytic properties, their relatively high preparation and acquisition costs can limit their attractiveness for low-cost biomass conversion. Natural zeolite therefore represents a potentially economical alternative because of its availability and lower cost. However, natural zeolite generally exhibits different surface properties, pore characteristics, and catalytic activity compared with highly engineered synthetic zeolites. Khan et al. demonstrated that natural zeolite and HZSM-5 produced different transformations of oxygenated compounds and hydrocarbon selectivities during biomass pyrolysis, indicating that natural zeolite can provide catalytic functionality while its performance remains strongly dependent on its physicochemical characteristics and preparation method [13]. Acid activation has been reported as a method for modifying the composition and surface properties of natural zeolites. However, the extent to which these changes affect catalytic activity depends on the initial mineral composition and activation conditions. Studies using natural catalysts further indicate that their catalytic performance depends on the interaction between catalyst characteristics and pyrolysis conditions [14].

Recent research on tobacco-stem catalytic pyrolysis has increasingly emphasized advanced catalyst engineering rather than low-cost process optimization. Metal-supported biochar catalysts have been investigated for selective production of phenolic compounds and hydrogen-rich gas, while hierarchical HZSM-5 has been reported to improve hydrocarbon and monocyclic aromatic selectivity through changes in catalyst structure and acidity [7],

[9]. More recently, ZIF-67/ZSM-5 dual-catalyst systems have been developed to selectively enrich pyrrole compounds in tobacco-stem-derived bio-oil [8]. Although these studies demonstrate significant progress in catalyst design and product selectivity, they also indicate that much of the recent literature is directed toward sophisticated catalyst systems and specific molecular products. In contrast, the use of acid-activated natural zeolite as a low-cost catalyst combined with systematic optimization of the principal pyrolysis operating variables for tobacco stem remains comparatively less investigated.

Process optimization is particularly important because pyrolysis variables do not necessarily affect bio-oil production independently. Increasing temperature can enhance the decomposition of cellulose, hemicellulose, and lignin and increase vapor formation, whereas excessive thermal severity can promote secondary cracking of condensable vapors into permanent gases. Similarly, increasing catalyst loading can enhance vapor conversion through acid-catalyzed reactions, but excessive catalytic severity may further crack condensable products and reduce liquid yield. Therefore, the relationship between temperature, reaction time, catalyst loading, and bio-oil production is potentially nonlinear and cannot be adequately described by changing one factor at a time. Response Surface Methodology (RSM), particularly the Box–Behnken Design (BBD), provides an efficient statistical framework for simultaneously evaluating multiple variables, quadratic effects, and interaction terms while reducing the number of required experimental runs. RSM-BBD has previously been applied to catalytic pyrolysis to optimize temperature and catalyst-related parameters for pyrolytic liquid production [15–17].

However, an important research gap remains. Existing tobacco-stem pyrolysis studies have largely focused on pyrolysis mechanisms, nitrogen transformation, advanced catalyst development, or selective

production of particular chemical fractions [5,7–9]. Meanwhile, studies employing natural zeolite have primarily examined catalyst comparison and the transformation of oxygenated compounds in other biomass feedstocks [13]. Despite recent advances in tobacco-stem pyrolysis and catalyst development, further investigation is warranted into the relative effects of acid-activated natural-zeolite loading, pyrolysis temperature, and reaction time on distilled bio-oil yield using a multivariable statistical approach. Furthermore, optimization studies commonly emphasize bio-oil yield, whereas bulk physicochemical properties such as density, viscosity, and pH may respond differently to changes in process conditions. A process condition that maximizes liquid yield does not necessarily produce a bio-oil with correspondingly improved physicochemical characteristics. This distinction is particularly relevant for tobacco stem because its bio-oil contains complex oxygenated, phenolic, acidic, and nitrogen-containing compounds [5–6].

Accordingly, this study evaluates the effects of pyrolysis temperature, reaction time, and acid-activated natural-zeolite loading on distilled bio-oil yield using RSM-BBD. Density, kinematic viscosity, and pH are also measured as supplementary product-characterization responses, while FTIR and GC–MS are used to examine selected functional groups and tentatively identified organic compounds. Bio-oil yield, density, viscosity, and pH are evaluated as process responses, while FTIR and GC–MS are used to characterize the chemical features of the resulting bio-oil. RSM-BBD is employed to quantify the response behavior and identify a favorable operating condition within the investigated experimental range.

2. RESEARCH METHODS

2.1. Research Design

This study employed a laboratory-scale experimental approach to investigate the effects and interactions of pyrolysis temperature, reaction time, and activated natural-zeolite loading on the production

and selected physicochemical properties of bio-oil derived from tobacco stem. Response Surface Methodology (RSM) combined with a Box–Behnken Design (BBD) was used to design the experiments and evaluate the response behavior. The experimental design and statistical analysis were performed using Design-Expert version 13.

The investigated independent variables were pyrolysis temperature, reaction time, and activated natural-zeolite loading, while bio-oil yield, density, viscosity, and pH were selected as response variables. Throughout this manuscript, “zeolite loading” refers specifically to the mass loading of acid-activated natural zeolite relative to the initial biomass mass and is expressed in wt%. The experimental domain was established based on three levels for each factor: 350–550°C for temperature, 2–3 h for reaction time, and 0–20 wt% for zeolite loading. The experimental ranges were selected based on preliminary experiments and reported operating conditions for lignocellulosic and tobacco-stem pyrolysis [1,2,10]. The selected temperature range of 350–550°C was intended to evaluate product formation across different levels of thermal severity, while reaction time and zeolite loading were varied within the predefined experimental domain.

2.2. Feedstock Preparation

Tobacco stems obtained from Probolinggo, Indonesia, were used as the lignocellulosic feedstock. The stems were cut to approximately 3 cm × 1 cm × 0.5 cm and dried under sunlight for approximately 2 h. The moisture content was determined from the difference between the initial wet mass and the mass after drying. The resulting moisture content was 7.9 wt%, which was below the 10% threshold established for the experiments. The dried tobacco stems were subsequently weighed at 200 g per experimental run.

The lignocellulosic composition of the feedstock was determined using the Van Soest method. Acid detergent fiber (ADF) and neutral detergent fiber (NDF) were

determined gravimetrically, while hemicellulose was calculated from the difference between NDF and ADF. Cellulose was determined from the acid hydrolysis residue, and lignin was determined from the subsequent ash correction after furnace treatment.

2.3. Natural Zeolite Activation

Natural zeolite was chemically activated using sulfuric acid prior to its use as a catalyst. A total of 200 g of natural zeolite was contacted with 300 mL of 4 M H₂SO₄ solution (zeolite-to-acid-solution ratio of 1 g:1.5 mL). The mixture was stirred and heated at 60°C for 1 h. After activation, the zeolite was separated by filtration and washed with deionized water until a neutral pH was obtained. The activated material was subsequently dried in an oven at 105°C for 1 h.

The activated zeolite was subsequently mixed with the tobacco stem according to the zeolite-loading level specified by the experimental design. Zeolite loading was expressed as the mass of activated natural zeolite relative to the initial biomass mass (wt%).

2.4. Catalytic Pyrolysis Procedure

Catalytic pyrolysis was conducted using a laboratory-scale pyrolysis system consisting of a pyrolysis vessel, temperature controller, nitrogen supply, condenser, product collection vessel, and vacuum system. The system configuration included a nitrogen cylinder for oxygen displacement, a pyrolysis tank, condenser, cooling-water tank, product tank, and vacuum pump.

For each experimental run, 200 g of prepared tobacco stem was mixed with the predetermined amount of activated natural zeolite and transferred into the pyrolysis vessel. The vacuum and condenser systems were activated, followed by nitrogen purging for 30 s to displace oxygen from the reactor. The nitrogen valve was then closed and the temperature set point was adjusted according to the experimental design. The pyrolysis system was heated until the

specified process temperature was reached and maintained for the designated reaction time. The three independent variables and their corresponding experimental levels are presented in Table 1.

After completion of each pyrolysis run, the reactor was cooled to approximately 26–40°C. The resulting biochar was separated, while the mass and volume of the condensed liquid product were recorded. The pyrolysis system was subsequently cleaned using steam for approximately 30 min before the next run.

Table 1. Experimental factors used in the RSM-BBD design.

Factor	Unit	Low level	Center level	High level
Pyrolysis temperature (A)	°C	350	450	550
Reaction time (B)	h	2	2.5	3
Zeolite loading (C)	wt%	0	10	20

2.5. Bio-oil Separation

The condensed liquid obtained from pyrolysis was subjected to a simple distillation step prior to the main physicochemical analyses. The condensed liquid was transferred to a distillation flask and heated using a heating mantle at 105°C. The generated vapor was condensed using cooling water at approximately 28°C, and the distillate was collected separately. Heating was continued for approximately 30 min, after which the resulting bio-oil fraction was collected for characterization.

2.6. Bio-oil Characterization

2.6.1. Bio-oil Yield

In this study, bio-oil yield refers to the mass yield of the distilled liquid fraction obtained after the separation step. Bio-oil yield was calculated gravimetrically based on the mass of bio-oil obtained relative to the initial mass of tobacco stem:

$$Y_{\text{bio-oil}}(\%) = \frac{m_{\text{bio-oil}}}{m_{\text{feedstock}}} \times 100 \quad (2)$$

where $m_{\text{bio-oil}}$ is the mass of the bio-oil obtained after the separation step and $m_{\text{feedstock}}$ is the initial mass of tobacco stem.

The reported yield represents the mass of the collected distillate relative to the initial mass of tobacco stem. It therefore describes the yield of the distilled liquid fraction rather than the total condensable liquid produced during pyrolysis.

2.6.2. Density

Bio-oil density was determined gravimetrically using a pycnometer at 20°C. The density was calculated from the difference between the mass of the filled and empty pycnometer divided by the pycnometer volume.

2.6.3. Viscosity

The kinematic viscosity of the bio-oil was measured using an Ostwald viscometer at 40°C. The flow time of the sample between the specified reference marks was recorded and used with the viscometer constant to calculate the viscosity.

2.6.4. pH

The pH of the bio-oil was measured using a calibrated pH meter. The instrument was calibrated using pH 4 and pH 10 buffer solutions before measurement. The bio-oil sample was homogenized and equilibrated to the calibration temperature before the electrode was immersed in the sample. The stable reading was then recorded.

2.7. Feedstock and Bio-oil Chemical Characterization

2.7.1. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the major functional groups present in the tobacco stem and resulting bio-oil. The analysis employed a Bruker ALPHA II FTIR spectrometer equipped with an ATR

sampling accessory. The reported spectral range was 4000–400 cm^{-1} , with a spectral resolution of up to 2 cm^{-1} .

FTIR data were used as supporting evidence for changes in the functional groups associated with the lignocellulosic feedstock and the resulting pyrolysis product.

2.7.2. GC-MS Analysis

Gas Chromatography–Mass Spectrometry (GC-MS) was employed to characterize the organic compounds present in the bio-oil. The analysis was performed using a Shimadzu GCMS-QP2020 NX system. The GC-MS data were used primarily to identify the chemical constituents of the selected bio-oil sample.

2.8. Experimental Design and Statistical Analysis

The experimental design was developed using Response Surface Methodology (RSM) with a Box–Behnken Design (BBD) implemented in Design-Expert version 13. Three independent variables were considered: pyrolysis temperature (A), reaction time (B), and zeolite loading (C). The corresponding response variables were bio-oil yield, density, viscosity, and pH. A three-factor Box–Behnken design consisting of 14 experimental runs, including two replicated center points, was employed.

A second-order polynomial model was used to describe the relationship between the independent variables and each response:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i < j} \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

where Y represents the predicted response, β_0 is the intercept, β_i and β_{ii} represent the linear and quadratic coefficients, respectively, β_{ij} represents the interaction coefficient, and ε represents the experimental error.

The experimental responses obtained from each run were entered into the Design-Expert model for analysis. ANOVA was

used to evaluate the statistical significance of the fitted quadratic models and their individual terms. Response-surface plots were subsequently generated to visualize the interaction between pairs of process variables.

For the optimization step, numerical desirability analysis was used to determine the combination of temperature, reaction time, and zeolite loading that simultaneously satisfied the specified response criteria. The software generated the predicted response values and the corresponding overall desirability.

3. RESULTS AND DISCUSSION

The results are discussed in terms of feedstock characteristics, bio-oil yield, statistical identification of the most statistically influential factor within the investigated domain for bio-oil yield, physicochemical properties, molecular composition, and numerical optimization. Particular attention is given to the role of activated natural-zeolite loading because it was identified as the most statistically influential factor affecting bio-oil yield. The experimental results obtained from the BBD runs are presented in Table 2.

3.1. Feedstock Characteristics and Its Pyrolysis Potential

Van Soest analysis showed that the tobacco stems collected from Probolinggo contained 42% cellulose, 16% hemicellulose, and 16% lignin, corresponding to a total lignocellulosic fraction of 74%. The remaining 26% was not individually resolved and may include non-structural and extractive fractions, moisture, and inorganic material that influence pyrolysis behavior and volatile compound formation. The relatively high lignocellulosic fraction indicates the suitability of the feedstock for thermochemical conversion.

The cellulose and hemicellulose fractions are primarily associated with oxygenated products, whereas lignin contributes substantially to phenolic and aromatic compounds during pyrolysis [1,18].

Table 2. Experimental data for the pyrolysis of tobacco stem to produce bio-oil.

	Factor 1 (A)	Factor 2 (B)	Factor 3 (C)	Response 1	Response 2	Response 3	Response 4
Run	Pyrolysis Temperature (°C)	Reaction Time (h)	Zeolite loading (wt%)	Distilled bio-oil yield (wt%)	Density (kg/dm ³)	Viscosity (mm ² /s)	pH
1	350	2	10	49.9284	0.9936	1.1415	4.62
2	550	3	10	68.7930	0.9970	1.0461	4.18
3	550	2.5	0	26.8326	0.9938	1.0543	4.33
4	450	3	0	15.4721	0.9982	1.1190	4.88
5	550	2.5	20	49.9700	0.9994	1.0752	4.49
6	450	2.5	10	66.1826	0.9878	1.0355	4.44
7	450	2	0	22.8915	1.0174	1.2387	4.58
8	350	2.5	0	37.5825	1.0022	1.1450	4.31
9	550	2	10	61.1826	0.9890	0.9729	5.42
10	450	2	20	41.9748	0.9994	1.0663	4.50
11	350	3	10	54.9010	0.9982	1.0543	4.65
12	450	2.5	10	64.4127	0.9834	1.0140	4.34
13	350	2.5	20	52.1142	0.9974	1.0673	4.79
14	450	3	20	54.2384	0.9952	1.0201	5.20

In addition, the presence of tobacco-specific nitrogen-containing constituents is expected to contribute to nitrogenous compounds in the resulting bio-oil [5,18]. These compositional characteristics provide a basis for interpreting the yield and molecular composition of the resulting bio-oil.

The feedstock composition also provides an important basis for interpreting the functional groups observed in the FTIR spectra. In particular, the presence of lignin is associated with the formation of phenolic compounds, whereas the cellulose and hemicellulose fractions contribute substantially to oxygenated compounds in the liquid product. Given these feedstock characteristics, the effect of the investigated pyrolysis conditions on bio-oil formation was subsequently evaluated.

3.2. Effect of Process Conditions on Bio-oil Yield

The experimental results showed that distilled bio-oil yield varied across the investigated combinations of pyrolysis temperature, reaction time, and zeolite loading. For example, the highest

experimental yield of 68.79 wt% was obtained at 550°C, 3 h, and 10 wt% zeolite, whereas the lowest yield of 15.47 wt% was obtained at 450°C, 3 h, without zeolite. Because these experimental conditions differ in more than one factor, this comparison describes the overall variation in yield rather than the isolated effect of zeolite loading. The individual and nonlinear contributions of the process variables were therefore evaluated using the fitted RSM model and response-surface plots. A similar non-monotonic response was observed at other conditions. These results indicate that the effect of zeolite loading was not linear. This behavior is consistent with previous studies showing that temperature, catalyst characteristics, zeolite loading, residence time, and reactor configuration influence the balance between primary biomass decomposition, vapor formation, secondary cracking, and condensation during catalytic pyrolysis [1,2]. Previous studies have reported that catalyst acidity and pore structure can influence vapor conversion, secondary cracking, and the distribution of pyrolysis products. These mechanisms may

help explain the nonlinear response observed with zeolite loading in the present study. However, because the physicochemical properties of the activated natural zeolite were not characterized, their specific contributions to the observed bio-oil yield cannot be directly established from the present experimental data.

The maximum yield obtained experimentally in the present study is comparable with previous tobacco-residue pyrolysis results. Khuenkao et al. reported a maximum bio-oil yield of approximately 55 wt% at 600°C during vacuum ablative pyrolysis of tobacco processing waste [4]. Ma et al. reported that the highest bio-oil productivity from waste tobacco stem occurred at approximately 600°C, although their overall product distribution was strongly affected by the formation of gas and char [5].

The relatively high liquid yield observed at 550°C in the present study can be associated with enhanced decomposition of the lignocellulosic matrix and increased volatilization of pyrolysis products. Nevertheless, increasing temperature does not necessarily increase bio-oil yield indefinitely. At excessive thermal severity, primary vapors may undergo secondary cracking, decarbonylation, decarboxylation, and reforming reactions, increasing the production of permanent gases at the expense of condensable products [1,2]. The observed nonlinear response to zeolite loading is consistent with possible changes in secondary vapor-conversion reactions. However, these mechanisms were not directly verified in this study because the catalyst properties and product-conversion pathways were not independently characterized.

This competing behavior indicates that bio-oil formation is governed by a balance between primary biomass decomposition and secondary vapor conversion, rather than by temperature alone. The experimental response ranges are summarized in Table 3.

Table 3. Experimental yield and selected physicochemical properties of distilled tobacco-stem bio-oil.

Properties	Experimental range
Bio-oil yield (wt%)	15.47–68.79
Viscosity at 40°C, mm ² /s	0.9729–1.2387
Density at 20°C, kg/dm ³	0.9834–1.0174
pH	4.18–5.42

Table 3 summarizes the experimental ranges of distilled bio-oil yield and selected physicochemical properties obtained in this study. Density, viscosity, and pH were measured to provide an initial characterization of the product. However, these parameters alone are insufficient to establish compliance with a commercial fuel specification or to confirm suitability for a specific fuel application. Because the intended end use of the product has not yet been established and the complete set of application-specific properties was not measured, the results are interpreted as an initial characterization of distilled tobacco-stem pyrolysis bio-oil rather than as evidence of fuel-grade quality.

3.3. RSM Model and Identification of the Most Statistically Influential Factor for Bio-Oil Yield

Among the investigated model terms, the linear and quadratic terms of zeolite loading were statistically significant in the fitted bio-oil-yield model ($p = 0.0121$ and $p = 0.0049$, respectively). These results indicate that zeolite loading was an important factor associated with yield variation within the investigated experimental domain.

The quadratic model was statistically significant ($p = 0.0474$), while the linear and quadratic terms of zeolite loading were significant ($p = 0.0121$ and 0.0049 , respectively).

The significance of both C and C^2 indicates a nonlinear response, consistent with the

experimental observation that increasing zeolite loading did not continuously increase bio-oil yield. The observed nonlinear response is consistent with the catalytic behavior commonly reported for acidic zeolite catalysts, in which moderate zeolite loading can enhance vapor conversion, whereas excessive catalytic severity may promote secondary cracking of condensable products [11,12].

The present finding is particularly relevant because natural zeolite represents a potentially lower-cost alternative to highly engineered synthetic zeolites. Khan et al. demonstrated that natural zeolite has different physicochemical properties from HZSM-5 and consequently exhibits different oxygenate conversion and hydrocarbon selectivity [13]. More recent research using natural-zeolite-based catalysts also confirms that catalyst acidity and pore structure can influence the balance between liquid-product formation, cracking, aromatization, and coke formation [19].

Therefore, the significant quadratic effect of zeolite loading observed in the present study should not be interpreted simply as evidence that a higher catalyst dosage is preferable. Instead, the results suggest the existence of a catalyst-loading window in which vapor upgrading is sufficiently promoted without excessive secondary cracking.

3.4. Effect of Temperature, Reaction Time, and Zeolite Loading: RSM and ANOVA

The RSM analysis provides a quantitative assessment of the process variables. Within the fitted model, the linear and quadratic terms for zeolite loading provided the clearest statistical evidence of an association with bio-oil yield. The effects of temperature, reaction time, and their interactions were not statistically significant at the 5% significance level. These findings apply only to the investigated experimental domain and should not be interpreted as evidence that temperature and reaction time are generally unimportant in pyrolysis. This indicates that their effects could not be

adequately represented as independent linear contributions within the investigated experimental domain. The ANOVA summary for the four response models is presented in Table 4.

The quadratic model used in this study for bio-oil yield was formulated as follows:

$$Y = -107.86568 - 0.101462A + 134.35050B + 2.63845C + 0.013189AB + 0.002151AC + 0.984150BC + 0.000069A^2 - 29.15405B^2 - 0.243649C^2 \quad (3)$$

where Y is the predicted distilled bio-oil yield (wt%), A is pyrolysis temperature (°C), B is reaction time (h), and C is activated natural-zeolite loading (wt%).

The different statistical responses demonstrate that the three process variables did not influence all bio-oil properties in the same manner.

Table 4. ANOVA summary for the RSM models.

Response	Model p-value	Model significance	Term with lowest p-value
Bio-oil Yield	0.0474	Significant	C, p = 0.0121
Density	0.4934	Not significant	C ² , p = 0.0715
Viscosity	0.2372	Not significant	C, p = 0.0808
pH	0.7641	Not significant	AB, p = 0.1989

Note: For density, viscosity, and pH, none of the listed individual terms was statistically significant at $\alpha = 0.05$.

Temperature is generally regarded as one of the most important variables in biomass pyrolysis. However, within the present experimental domain, its linear contribution to bio-oil yield was not statistically significant. Once sufficient thermal energy

is available for substantial lignocellulosic decomposition, catalyst-mediated secondary vapor reactions may become important determinants of the amount and composition of condensable products [7–9].

The significant quadratic catalyst term further demonstrates that the catalyst effect cannot adequately be described by a linear relationship. This finding supports the use of RSM as an appropriate process-engineering tool because it allows nonlinear effects to be quantified within the investigated experimental domain. Previous BBD studies have similarly demonstrated the usefulness of RSM for simultaneously evaluating temperature and catalyst-related parameters in catalytic pyrolysis [15–17].

Within the investigated range, bio-oil yield was more responsive to zeolite loading than to temperature or reaction time. The nonlinear response to zeolite loading suggests that excessive catalyst addition may promote secondary cracking of condensable products. None of the fitted two-factor interaction terms was statistically significant at $\alpha = 0.05$. Therefore, the present data do not provide sufficient statistical evidence of interaction effects within the investigated experimental domain.

The detailed ANOVA results for the bio-oil-yield model are presented in Table 5. The corresponding response-surface plots are shown in Figure 1.

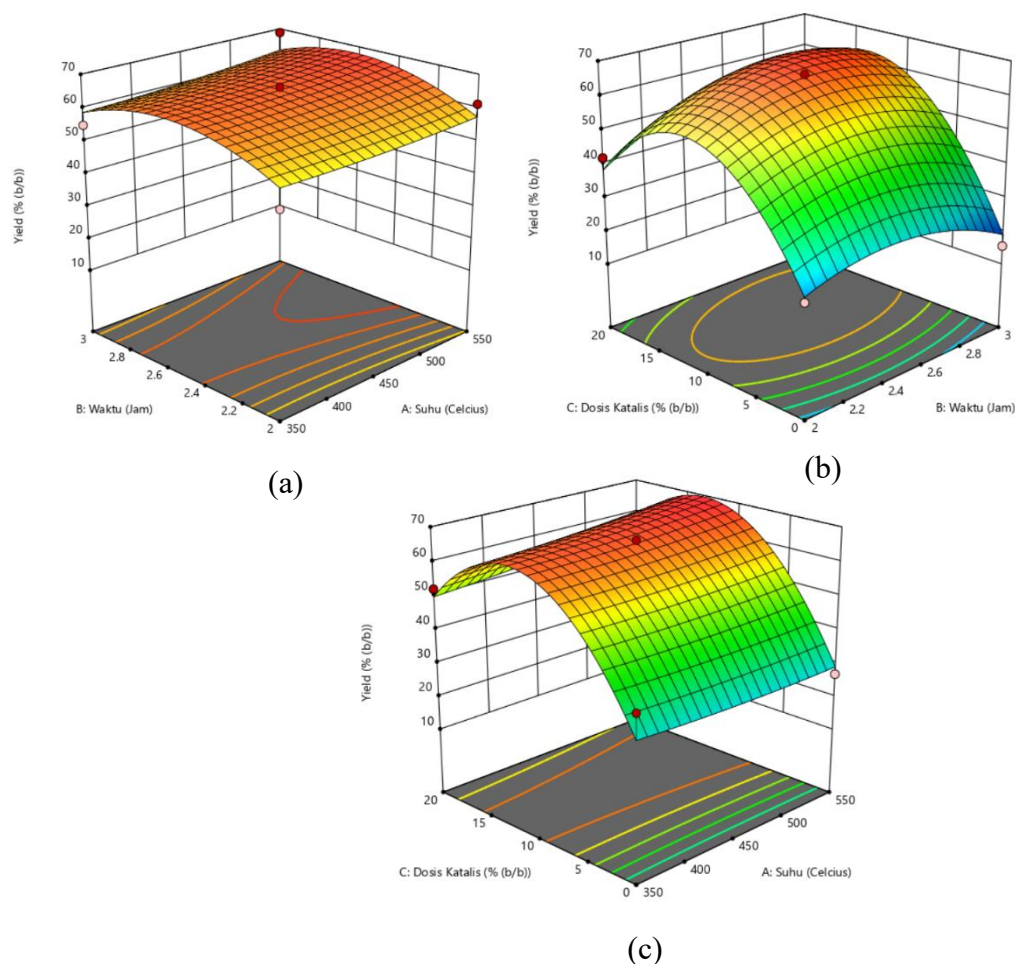


Figure 1. Response-surface plots showing the effects of (a) pyrolysis temperature and reaction time, (b) reaction time and activated natural-zeolite loading, and (c) activated natural-zeolite loading and pyrolysis temperature on distilled bio-oil yield.

Table 5. ANOVA results for the quadratic model of bio-oil yield using Design-Expert 13.

Source	Sum of Squares	DF	Mean Square	F Value	P Value	Remarks
Model	3355.55	9	372.84	6.19	0.0474	Significant
A	18.76	1	18.76	0.3116	0.6064	
B	37.96	1	37.96	0.6305	0.4716	
C	1140.48	1	1140.48	18.94	0.0121	
AB	1.74	1	1.74	0.0289	0.8733	
AC	18.51	1	18.51	0.3075	0.6088	
BC	96.86	1	96.86	1.61	0.2735	
A ²	1.53	1	1.53	0.0255	0.8810	
B ²	169.99	1	169.99	2.82	0.1682	
C ²	1899.68	1	1899.68	31.55	0.0049	
Residual	240.84	4	60.21			
Lack of Fit	239.28	3	79.76	50.92	0.1026	not significant
Pure Error	1.57	1	1.57			
Cor Total	3596.39	13				

The lack-of-fit test was not statistically significant at $\alpha = 0.05$ ($p = 0.1026$). However, this result should be interpreted cautiously because the pure-error estimate was based on limited replication. Model adequacy should therefore also be assessed using the coefficient-of-determination statistics and residual diagnostics.

3.5. Physicochemical Properties of Bio-oil

3.5.1. Density

The distilled bio-oil density ranged from 0.9834 to 1.0174 kg/dm³. Although some experimental conditions showed lower density at higher temperature or zeolite loading, the quadratic model was not statistically significant ($p = 0.4934$). These variations should therefore be interpreted as experimental trends rather than statistically confirmed effects.

The observed density values fall within a relatively narrow range compared with the variation in bio-oil yield. Thus, the present results indicate that yield optimization and density modification are not necessarily coupled responses.

3.5.2. Viscosity

The absence of a statistically significant viscosity model indicates that the effects of

the investigated variables could not be established within the present experimental domain. Bio-oil viscosity can depend on several compositional properties, including molecular-weight distribution and water content [20], but these factors were not independently evaluated in this study.

Consequently, the present data support a more cautious conclusion: activated natural-zeolite loading significantly influenced bio-oil yield but did not produce a statistically confirmed effect on viscosity.

This distinction is important because increasing liquid yield does not necessarily imply a proportional improvement in fuel-related properties.

3.5.3. pH

The distilled bio-oil exhibited pH values of 4.18–5.42, indicating an acidic liquid product. The acidic pH readings were accompanied by tentative GC–MS library assignments to acetic acid and propanoic acid. However, the present data do not establish a direct quantitative relationship between these compounds and the measured pH.

However, the quadratic model was not statistically significant ($p = 0.7641$),

indicating that the investigated variables did not significantly affect the measured pH.

The persistence of an acidic pH despite catalytic treatment indicates that acid-forming compounds remained in the distilled bio-oil. Further molecular characterization by FTIR and GC-MS was therefore used to examine the chemical features responsible for this behavior.

3.6. Molecular Characteristics of Bio-oil

3.6.1. FTIR Analysis

The FTIR spectra of the tobacco stem and selected bio-oil samples are presented in Figure 2, while the corresponding peak assignments are summarized in Table 6. The broad band around 3300 cm^{-1} was associated with O–H/N–H stretching, the band at 2854 cm^{-1} with aliphatic C–H stretching, and signals at $1636\text{--}1615\text{ cm}^{-1}$ with aromatic C=C structures. Bands at 1086 and 1026 cm^{-1} were assigned to C–O–C stretching, while the band near 896 cm^{-1} was associated with β -glycosidic structures characteristic of the lignocellulosic feedstock.

Table 6. FTIR peak assignments of tobacco stem and distilled bio-oil.

Observed wavenumber (cm^{-1})	Reference wavenumber range (cm^{-1})	Functional Group
3300	3223–3357	–OH and –NH
2854	2850–2910	C–H (aliphatic)
2182 and 2029	2200–2000	C $\equiv$ N (Unassigned; further verification required)
1636 and 1615	1600–1650	C=C aromatic
1319	1319	CH ₂
1086 and 1026	1000–1250	C–O–C (ether)
896	896	β -glycoside

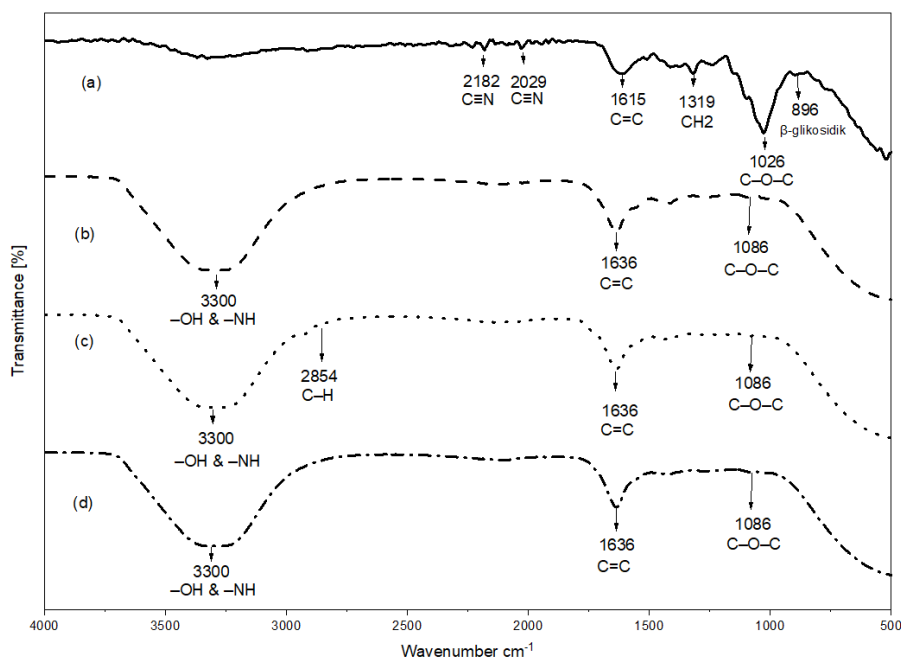


Figure 2. FTIR spectra of (a) tobacco stem and distilled bio-oil obtained at (b) 350°C , 2.5 h, and 0 wt% zeolite; (c) 350°C , 2.5 h, and 20 wt% zeolite; and (d) 450°C , 2.5 h, and 10 wt% zeolite.

These spectral features indicate that oxygenated and aromatic functionalities remained in the distilled bio-oil after catalytic pyrolysis [18].

The weak bands at 2182 and 2029 cm^{-1} could not be assigned unambiguously to specific functional groups due to possible overlapping or weak absorptions. Further spectral interpretation or complementary analysis is required to confirm their origin.

The persistence of oxygenated functionalities is reasonable considering the complexity of lignocellulosic pyrolysis. Although zeolite catalysts can promote dehydration, decarboxylation, decarbonylation, cracking, and aromatization, the extent of these reactions depends on catalyst properties, reactant accessibility, pore structure, acidity, and reaction severity [11,12].

This interpretation is consistent with tobacco pyrolysis studies reporting the formation of acids, phenols, ketones, alcohols, heterocyclic compounds, and nitrogen-containing species [5,18].

The FTIR spectra indicate that oxygen-containing functional groups remained detectable in the analyzed bio-oil samples. The present data do not establish the extent to which these functional groups were altered by zeolite loading.

3.6.2. GC-MS Analysis

GC-MS analysis was conducted on the bio-oil produced at 450°C, 2.5 h, and 10 wt% zeolite. Several compound classes, including acids, ketones, lactones, phenolics, methoxyphenols, and nitrogen-containing compounds, were tentatively identified, as shown in Figure 3 and summarized in Table 7. Because GC-MS library matching can be affected by sample preparation and analytical conditions, the identified compounds should be regarded as tentative unless supported by retention indices or authentic standards [21]. The library search assigned peaks to acetic acid, propanoic acid, 1-hydroxy-2-butanone, butyrolactone, phenol, 2-methoxyphenol, and nicotine. The largest chromatographic peak, accounting

for 51.68% of the reported peak area, was tentatively matched by the library search to 1,3-difluoro-2-propanol. Because this assignment is not supported by the known feedstock or reagents, the compound identity remains unverified. Accordingly, this peak is excluded from the chemical interpretation of the bio-oil until its identity can be independently confirmed.

Table 7. Tentatively identified compounds in distilled bio-oil by GC-MS analysis at a process temperature of 450°C, reaction time of 2.5 h, and zeolite loading of 10 wt%.

Retention time	%Area	Component
1.490	51.68	<i>Unverified library identification: 1,3-Difluoro-2-propanol</i>
1.863	8.00	Acetic acid
2.208	1.67	Propane, 2,2-dimethoxy-
2.286	2.30	N-Nitrosodimethylamine
2.434	2.04	Propanoic acid
2.722	0.94	Butanoic acid, methyl ester
3.087	7.22	2,2-Dimethoxybutane
3.209	1.78	1-Hydroxy-2-butanone
4.153	2.64	3,3-Dimethoxy-2-butanone
4.253	2.04	1,3-Dioxolane-4-methanol, 2-ethyl-
4.334	1.72	2-Furanmethanol
5.220	1.41	Butyrolactone
6.022	1.00	2-Cyclopenten-1-one, 3-methyl-
6.293	1.05	Phenol
6.427	0.78	Decane
6.973	2.20	1,2-Cyclopentanedione, 3-methyl-
7.962	1.77	Phenol, 2-methoxy-Nicotine, Pyridine, 3-(1-methyl-2-pyrrolidiny!)
11.742	9.77	

Note: Peak-area percentages represent relative chromatographic peak areas and should not be interpreted as absolute mass fractions or concentrations. Compound assignments are tentative library matches unless independently confirmed.

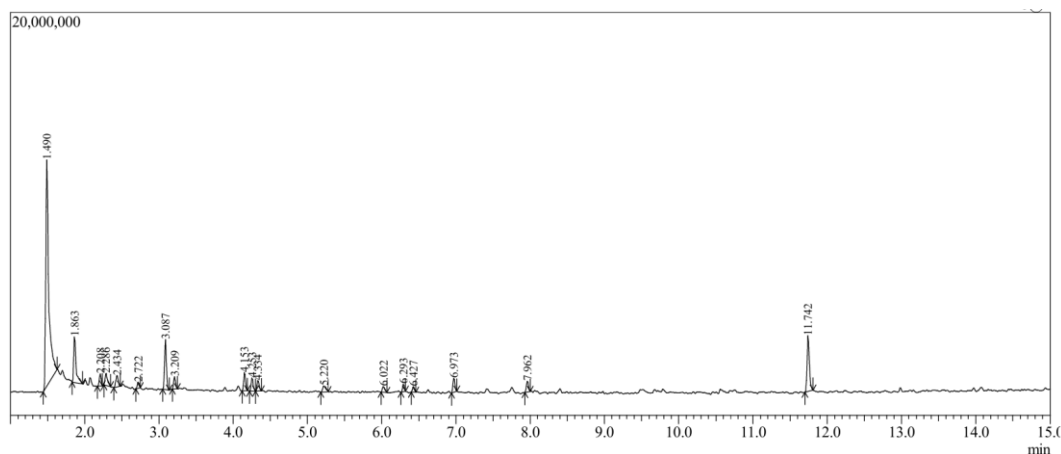


Figure 3. GC–MS chromatogram of distilled bio-oil produced at 450°C, 2.5 h, and 10 wt% zeolite loading.

The tentatively identified compounds reflect contributions from different lignocellulosic fractions. Acids, ketones, furans, and lactones are primarily associated with carbohydrate-derived pathways, whereas phenol and methoxyphenol are commonly associated with lignin decomposition. The GC–MS library search tentatively assigned a peak to nicotine, which is consistent with previous reports of nitrogen-containing products from tobacco-stem pyrolysis [5,18]. This assignment should be interpreted as provisional in the absence of confirmation using an authentic standard or complementary analytical evidence.

The detection of nicotine is particularly relevant to tobacco-stem pyrolysis because tobacco-specific nitrogen-containing compounds contribute to the distinctive chemical characteristics of tobacco-derived bio-oil. Ma et al. reported substantial nitrogen-containing products during tobacco-stem pyrolysis, while Bai et al. demonstrated that modification of the pyrolysis pathway through co-pyrolysis can substantially reduce nitrogen-containing compounds in tobacco-derived bio-oil [5,6]. The molecular composition obtained in this study is therefore broadly consistent with the complex chemical characteristics reported for tobacco-derived pyrolysis oils. Other studies have approached the problem from a process rather than catalyst-design perspective. Two-stage pyrolysis of tobacco

stem has been demonstrated to reduce tar and alter the distribution of gas and liquid products, while catalytic co-pyrolysis with corn stalk has been investigated to reduce nitrogen and oxygen contents in the bio-oil [6,10,22].

This distinction is important because natural zeolite does not necessarily provide the same molecular selectivity as hierarchical HZSM-5 or metal-supported catalysts. Its potential advantage lies in combining catalytic functionality with comparatively low-cost catalyst availability [13,19]. The statistical model and product characterization were subsequently integrated to identify a favorable operating condition for bio-oil production.

3.7. Numerical Optimization and Predicted Operating Condition

Numerical desirability analysis identified favorable operating conditions, with the predicted responses presented in Table 8 and the optimization criteria and boundary conditions summarized in Table 9.

The model predicted a favorable condition of 527.70°C, 2.55 h, and 12.36 wt% zeolite, with a predicted bio-oil yield of 69.08 wt%. The predicted yield of 69.08 wt% is slightly above the maximum observed experimental yield of 68.79 wt%.

Table 8. Model-predicted operating condition Based on Design-Expert Version 13 (DoE V13).

Parameter	Model-predicted condition
Temperature, °C	527.70
Reaction time, h	2.55
Zeolite loading, wt%	12.36
Bio-oil yield, wt%	69.08
Density, kg/dm ³	0.9863
Viscosity, mm ² /s	1.0003
pH	4.39
Desirability	1

This difference represents a model prediction and should not be interpreted as an experimentally demonstrated increase in yield. The intermediate zeolite loading also agrees with the significant quadratic effect of catalyst loading. The desirability value of 1.00 reflects the optimization criteria defined in the software and does not indicate perfect predictive accuracy or confirmed product quality. The predicted operating condition requires experimental validation. The numerical optimization primarily aimed to maximize distilled bio-oil yield while keeping the process variables within the

investigated ranges. Density, viscosity, and pH were not included as optimization criteria because their fitted response models were not statistically significant. Therefore, the predicted condition should be regarded as a favorable operating condition rather than a confirmed optimum and requires experimental validation.

The application of RSM for identifying an operating region is consistent with previous pyrolysis studies. Oyebanji et al. used BBD to simultaneously investigate temperature and biomass-to-catalyst ratio [15], while Amrullah et al. demonstrated the application of RSM for simultaneous consideration of pyrolysis conditions and bio-oil production and quality [16]. Similar RSM-based optimization has also been demonstrated for pilot-scale biomass pyrolysis [17].

The numerical optimization was performed using Design-Expert (DOE) based on the investigated experimental domain and the response criteria specified in Table 9. The lower and upper limits for bio-oil yield were defined according to the minimum and maximum experimental yields obtained in this study, whereas the process-factor boundaries were set within the investigated ranges. The predicted operating conditions and corresponding responses generated by the optimization run are presented in Table 8. These values represent model predictions and should not be interpreted as experimentally validated results.

Table 9. Response criteria and boundary conditions used in numerical desirability analysis.

Factor/Response	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight
Temperature, °C	In range	350	550	1	1
Reaction time, h	In range	2	3	1	1
Zeolite loading, wt%	In range	0	20	1	1
Bio-oil yield, wt%	Maximize	15.4721	68.793	1	1
Density, kg/dm ³	None	-	-	-	-
Viscosity, mm ² /s	None	-	-	-	-
pH	None	-	-	-	-

3.8. Integrated Process Interpretation

The results show that the fitted bio-oil-yield model and the models for density, viscosity, and pH differed in statistical significance. Within the investigated domain, zeolite loading exhibited significant linear and quadratic effects on distilled bio-oil yield, whereas the physicochemical-property models were not statistically significant. These findings indicate that the process variables could not be shown to affect all measured responses in the same way.

This difference is consistent with the complex nature of pyrolysis, in which changes in operating conditions can affect product formation without necessarily producing proportional changes in bulk physicochemical properties [1,2,11,12,20].

FTIR indicated the presence of selected oxygen-containing functional groups, while GC–MS library searches tentatively assigned several peaks to acids, phenolics, and nitrogen-containing compounds. These findings provide an initial characterization of the distilled bio-oil rather than a comprehensive or definitive identification of its molecular composition. These compounds are associated with the decomposition and transformation of cellulose, hemicellulose, lignin, and tobacco-specific components during pyrolysis [5,18,21]. The results therefore support the view that bio-oil quality is governed by its molecular composition rather than yield alone.

The condition of 527.70°C, 2.55 h, and 12.36 wt% zeolite is a model-predicted candidate for achieving a high distilled bio-oil yield within the investigated domain. Its performance remains to be confirmed experimentally. However, it should not be regarded as a confirmed optimum because the predicted condition has not yet been experimentally validated. The use of RSM for identifying favorable operating regions is consistent with previous biomass pyrolysis studies [15–17].

A limitation of the present study is that detailed physicochemical characterization of the raw and acid-activated natural zeolite

was not performed. Consequently, the observed effect of zeolite loading on bio-oil yield cannot be directly attributed to specific catalyst properties, such as acidity, surface area, pore structure, or mineral composition. The proposed catalytic pathways are therefore interpreted based on previous studies rather than as experimentally verified mechanisms in the present work. Further catalyst characterization would be required to establish the relationship between catalyst properties, process conditions, and product formation.

4. CONCLUSION

Under the investigated conditions, the distilled bio-oil yield ranged from 15.47 to 68.79 wt%, with the highest experimental yield obtained at 550°C, a reaction time of 3 h, and a zeolite loading of 10 wt%. The fitted quadratic model for distilled bio-oil yield was statistically significant ($p = 0.0474$), and both the linear and quadratic terms of zeolite loading were statistically significant. These results indicate a nonlinear association between zeolite loading and distilled bio-oil yield within the investigated experimental domain. In contrast, the fitted models for density, viscosity, and pH were not statistically significant.

Numerical optimization identified a model-predicted candidate operating condition of 527.70°C, 2.55 h, and 12.36 wt% zeolite, with a predicted distilled bio-oil yield of 69.08 wt%. This condition should not be considered a confirmed optimum until experimentally validated.

FTIR analysis indicated the presence of selected functional groups in the distilled bio-oil, while GC–MS library searches provided tentative assignments for several compounds. Because some compound identifications remain unverified, the chemical characterization should be regarded as preliminary.

This study focused on process optimization and selected physicochemical and chemical characterization of the distilled bio-oil. The measured properties are insufficient to

establish compliance with commercial fuel specifications or suitability for a specific application. Further characterization, including calorific value and other application-specific properties, is therefore required to assess its potential use.

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AUTHOR CONTRIBUTIONS

C.E.L.: Conceptualization, Data curation, Validation, Writing – original draft, Writing – review & editing. **F.S.F.:** Investigation, Data curation. **T.S.:** Investigation, Data curation. **A.S.S.:** Data validation, Writing – review & editing. **R.D.C.:** Methodology, Formal analysis, Writing – review & editing. **H.D.:** Validation, Writing – review & editing. **M.A.I.I.:** Writing – review & editing. All authors read and approved the final manuscript.

CONFLICTS OF INTEREST

The authors declare no competing financial interests.

DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used OpenAI's ChatGPT to assist with language editing and to improve the clarity, conciseness, and readability of the manuscript. The authors critically reviewed and revised the AI-assisted text and take full responsibility for the accuracy, integrity, and final content of the published article.

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