Proceedings of the 6th ITB International Graduate School Conference
Multidisciplinary Collaboration for Sustainable Energy: Science, Technology, Policy, and Society

Kinetic Study of Bio-Oil Production from Pyrolysis of Rice Husk and Corncob Mixture Using Thermogravimetric Analysis

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Abstract. The efficient production of bio-oil from lignocellulosic biomass requires a deep understanding of pyrolysis kinetics, particularly during stages critical for bio-oil formation. This study investigates the pyrolytic behavior and kinetic parameters of a rice husk and corncob mixture (1:1 mass ratio), focusing on the decomposition phases that significantly influence bio-oil yield. Thermogravimetric analysis (TGA) was performed at heating rates of 10, 20, and 30 °C/min to analyze biomass decomposition process. Activation energy (Ea) was determined using the Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) isoconversional methods over a conversion range (α) of 0.1 to 0.6, corresponding to the primary degradation stage responsible for bio-oil production. The Coats-Redfern method was applied to identify the reaction mechanism in the α range of 0.2 to 0.6. Ea values calculated using the KAS and FWO methods ranged between 147 to 200 kJ/mol. The Diffusion 3D model, identified through the Coats-Redfern approach, showed Ea values consistent with those from the isoconversional methods. Cross-method validation and comparison with existing literature confirm the robustness of the kinetic parameters. These findings contribute to the design of sustainable energy production systems by providing updated kinetic insights for optimizing biomass pyrolysis processes at both laboratory and industrial scales.

Keywords: *activation energy; bio-oil; corncob; pyrolysis; reaction kinetics; rice husk; thermogravimetric analysis.*

1 Introduction

Lignocellulosic biomass has gained significant attention as a renewable energy source due to its abundance, carbon neutrality, and potential for producing high-

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value fuels through thermochemical processes [1]. Unlike synthetic polymers, biomass undergoes a multi-step thermal decomposition during pyrolysis, involving distinct temperature intervals for hemicellulose, cellulose, and lignin degradation. The specific composition and structural ratios of these biomass constituents significantly influence both the decomposition pathways and resultant product distributions [2].

Extensive research has identified promising biomass feedstocks capable of achieving high bio-oil yields, optimized conversion processes, and innovative technologies facilitating large-scale biomass utilization. Central to this development is a comprehensive understanding of pyrolysis kinetics, critical for transitioning laboratory-scale processes to industrial applications. Kinetic studies elucidate reaction pathways, determine activation energies, and quantify the influence of operational parameters such as temperature, heating rate, and catalyst usage [3].

A deeper understanding of biomass decomposition mechanisms is pivotal, not only for enhancing process efficiency but also for selecting appropriate kinetic models and designing reactors. Advanced simulation tools, such as Computational Fluid Dynamics (CFD), have significantly improved the design and optimization of pyrolysis reactors. Additionally, kinetic studies provide essential insights for broader applications, including material degradation and fire safety engineering [4].

Historically, kinetic studies predominantly utilized isothermal approaches. However, advancements in analytical techniques such as Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC) have increasingly favored non-isothermal methods. These modern techniques provide richer and more reliable kinetic data from single experimental runs, enhancing analytical accuracy [5,6].

To accurately interpret biomass pyrolysis, an understanding of its chemical and structural composition is essential. Typically, biomass comprises cellulose (38–50%), hemicellulose (23–32%), and lignin (15–25%), with additional extractives and inorganic components constituting 5–13%. Cellulose is a linear polymer consisting of glucose units, hemicellulose is an amorphous polymer composed of various sugar monomers, and lignin is a complex, phenolic macromolecule with a non-crystalline structure. Furthermore, inorganic constituents such as calcium, silicon, phosphorus, and potassium significantly impact pyrolysis behavior and product outcomes [7].

Pyrolysis, performed under oxygen-free conditions, converts biomass into valuable products such as bio-oil, syngas, and biochar [8]. Product distribution and efficiency depend heavily on operating parameters like temperature, residence time, and catalyst selection. Elevated pyrolysis temperatures typically enhance bio-oil and syngas production, while lower temperatures promote biochar generation. Catalysts, including Ni, Co, and zeolites, have demonstrated effectiveness in reducing activation energy, accelerating reaction rates, and improving the quality of bio-oil [9].

Due to biomass heterogeneity and overlapping decomposition reactions, biomass pyrolysis kinetics are inherently complex [10]. Various kinetic models, such as the Arrhenius equation and Distributed Activation Energy Model (DAEM), have been developed to predict reaction rates and product yields. Recent advances also incorporate machine learning algorithms with conventional kinetic models, significantly enhancing prediction accuracy and optimization potential [11].

Despite numerous studies on individual biomass types, limited kinetic information is available for biomass mixtures such as rice husk and corncob. This study aims to fill that gap by analyzing the pyrolysis behavior and kinetics of a 1:1 mixture using TGA and multiple kinetic models. The novelty lies in the cross-method validation and the identification of a dominant reaction mechanism specific to the mixture, which can support future reactor design and optimization efforts. To the best of the authors' knowledge, this is the first study that establishes 3D diffusion as the dominant kinetic model for a rice husk–corncob mixture, verified through both isoconversional and model-fitting methods.

2 Pyrolysis Mechanism

The pyrolysis of biomass occurs sequentially, beginning with moisture evaporation, followed by the thermal decomposition of its primary constituents: hemicellulose, cellulose, and lignin (Figure 1) [9]. Hemicellulose decomposition occurs typically between 250 and 350°C, producing various volatile organic compounds. Cellulose decomposes at slightly higher temperatures (approximately 325–400°C), predominantly releasing levoglucosan and other sugars [5]. In contrast, lignin undergoes decomposition over a broader temperature range (300–550°C), yielding phenolic compounds, biochar, and gaseous products [7].

Secondary pyrolysis reactions involve the cracking and recombination of volatile compounds. These reactions are significantly influenced by operational parameters such as temperature, heating rate, and vapor residence time [2]. Generally, higher pyrolysis temperatures enhance the production of bio-oil and syngas, while lower temperatures favor biochar formation [9]. Moreover, interactions between biomass components, particularly lignin's influence on levoglucosan polymerization, play an essential role in determining bio-oil quality [4].

Understanding these reaction mechanisms is crucial for optimizing pyrolysis processes to maximize biofuel yields and improve process efficiencies. Future research should concentrate on refining detailed reaction pathways and incorporating catalytic strategies to enhance selectivity, efficiency, and the overall quality of pyrolysis-derived products.

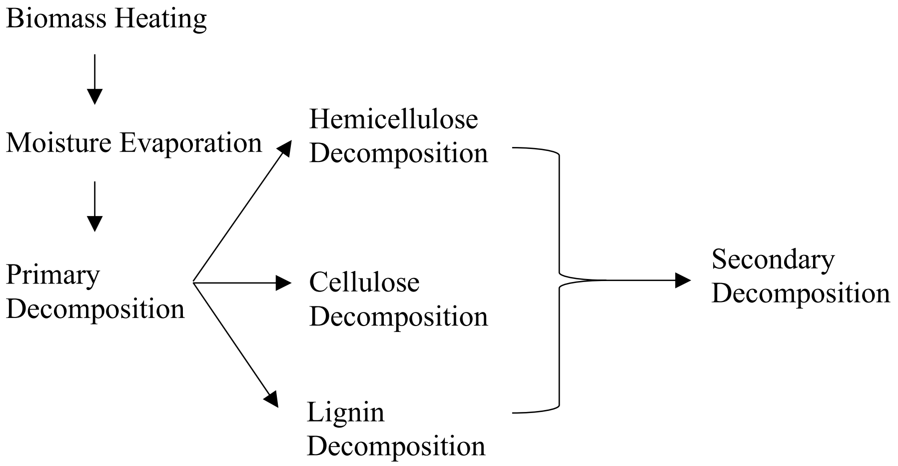


Figure 1 Stages of biomass pyrolysis decomposition

3 Kinetic models

Kinetic models are crucial for understanding and optimizing biomass pyrolysis processes. They provide insights into reaction mechanisms, activation energy, and product distribution, enabling better process control and reactor design. These models help predict reaction rates, conversion efficiencies, and product distributions under various conditions. The primary kinetic models used in biomass pyrolysis studies include Arrhenius-based models, Distributed Activation Energy Models (DAEM), power-law models, isoconversional methods, mechanistic models, machine learning approaches, computational fluid dynamics (CFD), and hybrid models.

Arrhenius-based models describe the temperature dependence of reaction rates, relying on parameters such as the pre-exponential factor and activation energy [1]. The Arrhenius equation is expressed as:

$$k=A\, exp^{\frac{-Ea}{RT}} \tag{1}$$

where k is the reaction rate constant, A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant, and T is the absolute temperature. While effective for simple reactions, these models may not fully capture the complexities of biomass pyrolysis, which involves multiple parallel and sequential reactions.

The DAEM, widely applied to model the thermal degradation of heterogeneous materials like biomass, assumes a distribution of activation energies rather than a single value, making it more representative of complex reactions [12]. The general form of DAEM is:

$$\alpha(T) = \int_0^\infty \left[1 - \exp\left(-A\exp\left(-\frac{E}{RT}\right)t\right)\right] f(E)dE \qquad (2)$$

where α(T) is the conversion degree, f(E) is the distribution function of activation energies, and t is the reaction time. This model provides a better fit for experimental data, especially when dealing with overlapping decomposition stages of hemicellulose, cellulose, and lignin.

Power-law models describe reaction kinetics based on the reaction order (n), with the general expression:

$$\left(\frac{d}{dt}\ \alpha\right) = \mathrm{k}(1- \alpha)\mathrm{n} \qquad (3)$$

where dα/dt is the rate of conversion, k is the reaction rate constant, and n is the reaction order. These models are useful for empirical data fitting, though they lack mechanistic detail for predictive modeling beyond experimental conditions [5].

Isoconversional methods, such as the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods, do not assume a specific reaction mechanism. Instead, they calculate the activation energy as a function of conversion, providing insights into the complexity of biomass decomposition [9].

Mechanistic models aim to describe the detailed chemical pathways and intermediate species formed during pyrolysis, often based on lumped kinetic schemes where complex reactions are grouped into a limited number of pseudocomponents, such as gas, tar, and char [7].

Recent advancements have introduced machine learning (ML) techniques to model biomass pyrolysis kinetics. ML algorithms, such as artificial neural networks (ANN), support vector machines (SVM), and random forests, can analyze large datasets to identify patterns and predict outcomes [5]. ANN models are capable of capturing nonlinear relationships between process parameters and product yields, while SVM and random forests are useful for classification and regression tasks related to biomass conversion efficiency.

CFD models integrate kinetic data with fluid dynamics to simulate pyrolysis reactors. These models provide spatial and temporal resolutions of temperature, velocity, and concentration fields, offering detailed insights into reactor performance and scale-up potential [12]. Hybrid models combine mechanistic and data-driven approaches to leverage the strengths of both, enhancing predictive accuracy and providing comprehensive insights into biomass pyrolysis processes [5].

Table 1 Influence of Pyrolysis Parameters on Product Yields

Parameter	Bio-oil Yield (%)	Syngas Yield (%)	Biochar Yield (%)	Reference
Temperature	50-70	15-30	10-20	Kan et al., 2016
Heating Rate	40-65	20-35	10-25	Hernowo et al., 2022
Catalyst Usage	55-75	10-25	10-15	Ciesielski et al., 2020
Residence Time	45-65	15-30	10-25	Anca-Couce, 2016

4 Methodology

4.1 Biomass Feedstock and Sample Preparation

The biomass mixture consisted of rice husk and corncob mixed at a 1:1 mass ratio. Samples were dried to a moisture content below 10% prior to testing.

4.2 Thermogravimetric Analysis (TGA)

TGA was conducted at heating rates of 10, 20, and 30 °C/min over a temperature range of 30–600 °C under a nitrogen atmosphere to ensure inert pyrolysis conditions. Mass loss data were recorded to calculate the degree of conversion (α). The initial (T_1) and final (T_2) temperatures marking the onset and completion of pyrolysis were determined based on TG/DTG and DSC data. T_1 was set at the temperature corresponding to the onset of significant mass loss, primarily from hemicellulose and cellulose decomposition (~250 °C). T_2 was defined as the temperature at which the mass loss rate significantly decreased, and the DSC peak flattened (~500 °C), signifying the primary stage for bio-oil production.

4.3 Determination of Kinetic Parameters

Activation energy (Ea) was calculated using the following approaches:

- Isoconversional Methods: KAS and FWO methods applied over $\alpha = 0.1$–0.6.
- Model Fitting Method: Coats-Redfern applied over $\alpha = 0.2$–0.6 to identify the dominant reaction mechanism. Reaction mechanisms evaluated included first-order, second-order, three-dimensional diffusion (Diffusion 3D), nucleation, and contracting surface models.

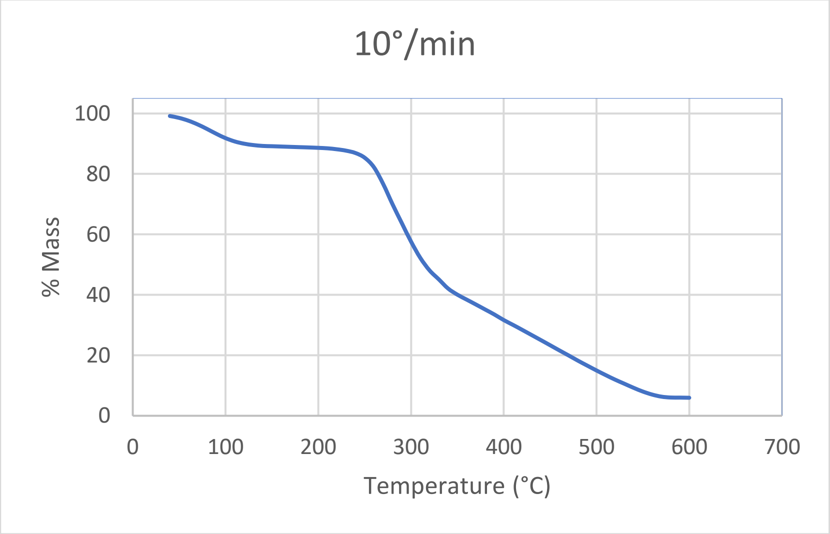
4.4 Model Validation

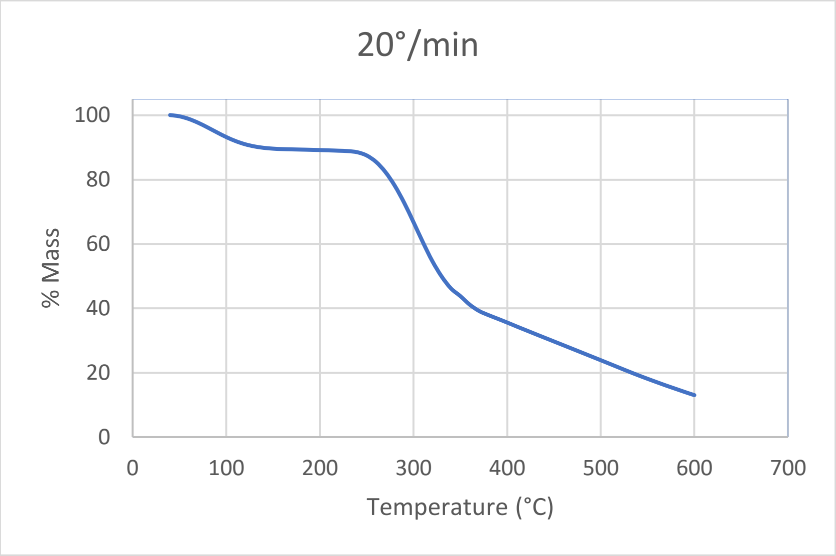
Validation of kinetic models involved cross-comparison of Ea values derived from different methods and benchmarking against relevant kinetic parameters reported in the literature.

5 Result and Discussion

5.1 Thermogravimetric Curves and Degree of Conversion

The TG and DTG curves (Figures 2 and 3) reveal a major mass loss between 250–500 °C, corresponding to the decomposition of hemicellulose, cellulose, and part of lignin—aligning with the main bio-oil production stage. Increasing the heating rate shifts the degradation curves toward higher temperatures due to thermal lag and diffusion resistance within biomass particles.





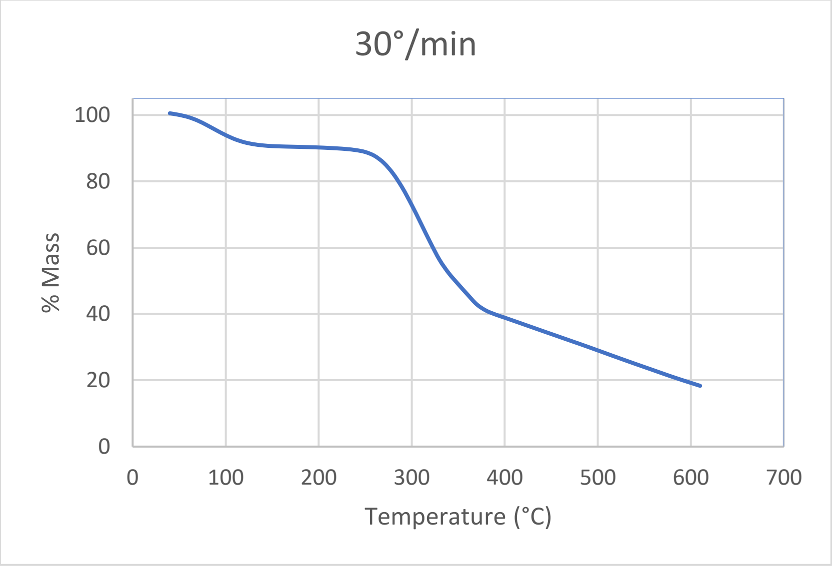
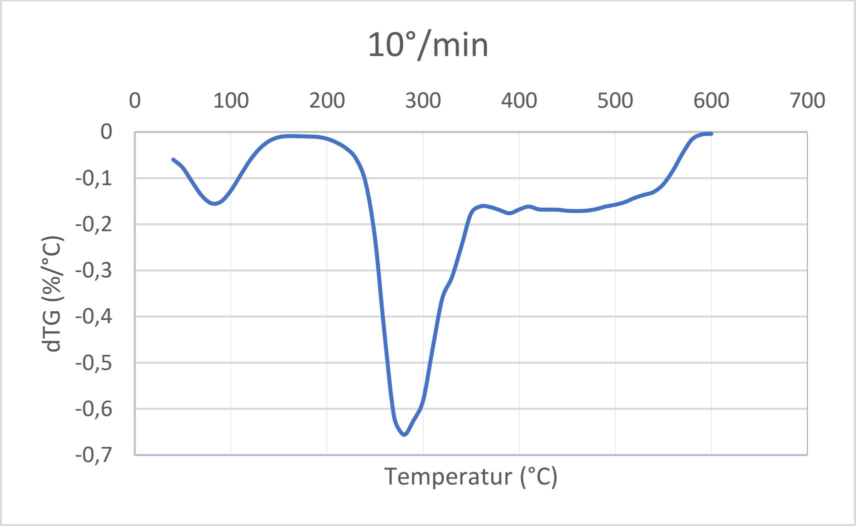
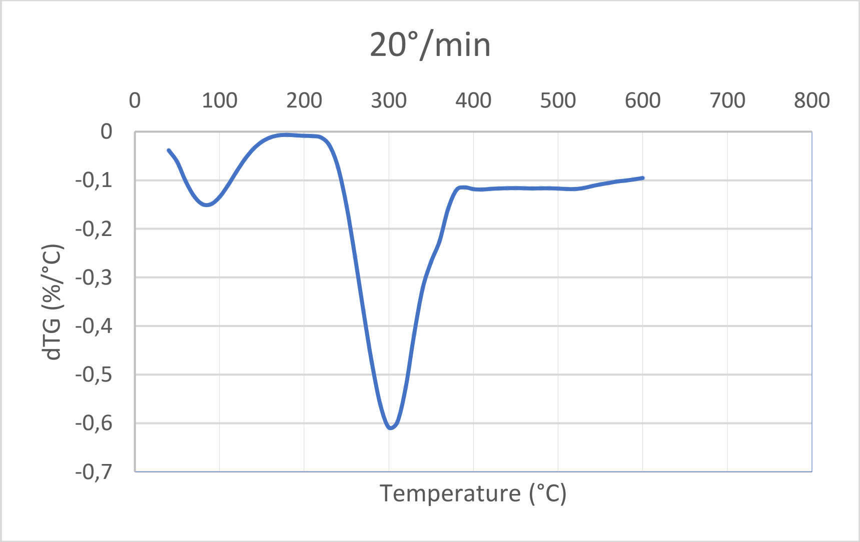


Figure 2 Thermogravimetric (TG) curves of the rice husk and corncob mixture at heating rates of 10, 20, and 30 °C/min


10°/min
0
100
200
300
400
500
600
700
0
-0,1
-0,2
-0,3
-0,4
-0,5
-0,6
-0,7
dTG (%/°C)
Temperatur (°C)


20°/min
0
100
200
300
400
500
600
700
800
0
-0,1
-0,2
-0,3
-0,4
-0,5
-0,6
-0,7
dTG (%/°C)
Temperature (°C)

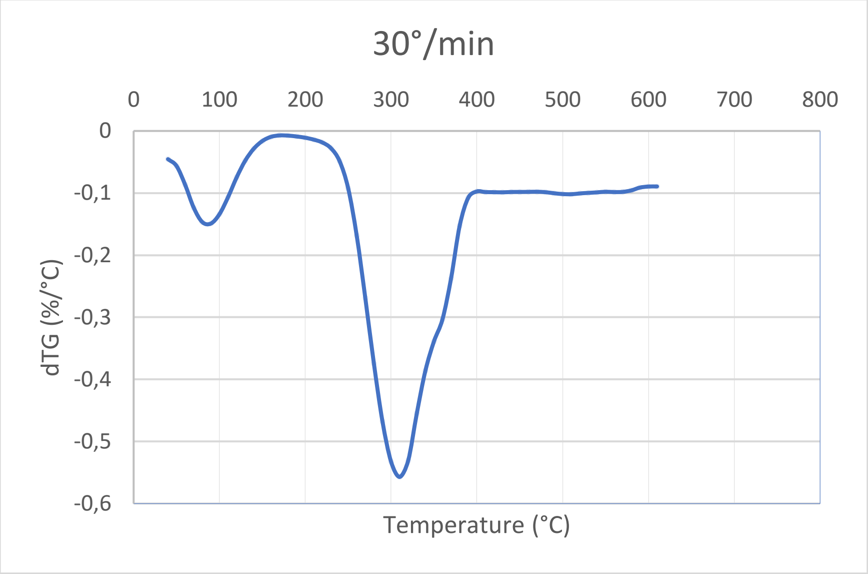


Figure 3 Derivative thermogravimetric (DTG) curves of the rice husk and corncob mixture at heating rates of 10, 20, and 30 °C/min

Table 2 summarizes the onset (T_1) and completion (T_2) temperatures of pyrolysis at different heating rates, derived from TG, DTG, and DSC data. The increasing trend of both T_1 and T_2 with higher heating rates reflects the influence of thermal lag. These temperatures were used to determine the effective range for kinetic modeling, confirming that the $\alpha = 0.1–0.6$ interval consistently covers the main volatile release phase across all heating rates.

Table 2 Initial and final pyrolysis temperatures

Heating Rate	T_1 (°C)	T_2 (°C)
10°C/min	245.2	450.1
20°C/min	248.8	460.1
30°C/min	251.3	470

The onset temperature T_1 was identified at the beginning of significant mass loss (≈245–251 °C), while T_2 was defined at the point where the DTG curve declined and the DSC signal leveled off (≈450–470 °C), marking the end of the primary devolatilization stage. This T_1–T_2 range characterizes the main bio-oil formation window.

Accordingly, the conversion range α = 0.1–0.6 was selected for kinetic modeling. This excludes early moisture evaporation (α < 0.1) and later solid-phase degradation leading to biochar (α > 0.6), capturing the most reactive phase relevant to bio-oil yield.

5.2 Kinetic Parameters from Isoconversional Methods

5.2.1 Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO)

Distinct trends in activation energy (Ea) values across the α range of 0.1–0.6 were identified and are detailed in Table 3. The coefficient of determination (R^2) values indicate strong linearity for all three methods, validating the reliability of the regression results. The high R^2 values (above 0.95) confirm the linearity of the regression results, indicating strong reliability of the applied kinetic models.

At low conversion levels (α = 0.1–0.3), higher Ea values were observed due to the decomposition of hemicellulose and amorphous cellulose, which requires substantial activation energy. As α increased, Ea declined as most reactive fractions decomposed, making the reaction easier. Beyond α = 0.4, Ea increased again, reflecting the involvement of crystalline cellulose and thermally stable lignin.

The Ea–α curves obtained from the KAS and FWO methods nearly overlapped, with maximum differences of less than 2 kJ/mol, indicating strong consistency between the two methods.

Table 3 Ea values calculated using the KAS and FWO methods

	KAS		**FWO**	
α	Ea	R^2	Ea	R^2
0.1	178.368556	0.994	178.210226	0.9946
0.2	151.248288	0.9998	152.602537	0.9998
0.3	147.881118	0.9999	149.566615	0.9999
0.4	155.72122	0.9975	157.180139	0.9978
0.5	168.574664	0.9908	169.568916	0.9918
0.6	200.500424	0.9555	200.133697	0.9595
Average Ea (kJ/mol)	**167.049045**		**167.877022**	
STD	19.9742162		19.147506	

5.3 Kinetic Parameters from the Coats-Redfern Method

Reaction mechanism models were evaluated using the Coats-Redfern method over $\alpha = 0.2$–0.6. The Diffusion 3D model produced Ea values of 146.68, 168.45, and 165.63 kJ/mol at heating rates of 10, 20, and 30 °C/min, respectively, resulting in an average Ea value of 160.25 kJ/mol.

The selection of the Diffusion 3D model was supported by:

1. Ea values close to those determined by the isoconversional methods, reinforcing their validity.
2. Reaction characteristics at intermediate to high α levels, where volatile release became limited by diffusion through the biomass particles, consistent with heterogeneous biomass pyrolysis theory.

5.4 Validation of Results

Cross-method validation demonstrated consistent Ea values between the KAS and FWO methods, supporting the reliability of the data. The Diffusion 3D model yielded Ea values that were realistic and closely matched those from the isoconversional analyses. The Ea values from KAS and FWO methods were within the range commonly reported for lignocellulosic biomass pyrolysis 147–200 kJ/mol ([13]; [14]; [15]; [16]). The kinetic parameters obtained also generated simulated α–T curves that closely matched the experimental data, confirming the accuracy of the results.

5.5 Interpretation of Activation Energy (Ea), Its Relation to the Biomass Mixture, and Research Implications

The Ea values obtained reflect the energy required to initiate and sustain the pyrolysis reactions. The range of 147–178 kJ/mol indicates moderate reactivity typical of lignocellulosic biomass for bio-oil production—sufficiently low to allow reactions at moderate temperatures (~400–500 °C), yet high enough to prevent uncontrolled reactions.

The observed kinetics reflect the reactivity of both rice husk and corncob. Their interaction further affects the overall decomposition behavior. The high silica content of rice husk contributed to diffusion resistance, while hemicellulose and cellulose from corncob provided reactive volatile fractions. This combination resulted in variable Ea profiles depending on which component dominated at specific reaction stages. The selection of the Diffusion 3D model supports the hypothesis that, at intermediate to high conversion levels, the release of volatile products was increasingly limited by internal mass transport, influenced by the physical structure of the biomass mixture.

This study makes a significant scientific contribution by providing specific kinetic data for a rice husk and corncob mixture, which are scarcely available in the literature, thereby expanding the kinetic database for biomass mixtures. Furthermore, identifying the dominant reaction mechanism (Diffusion 3D) enhances understanding of mass transport limitations during the bio-oil formation stage, informing particle and reactor design.

Cross-method validation and comparison with the literature confirmed that the applied kinetic approach is reliable and applicable to studies involving other biomass mixtures. The derived kinetic parameters can be utilized in reactor simulations to predict pyrolysis behavior under various temperatures and heating rates, facilitating the determination of optimal operating conditions to maximize bio-oil yield, minimize biochar and unwanted gas formation, and guide the development of laboratory- and industrial-scale reactors. These kinetic insights are particularly valuable for CFD-based reactor simulations, aiding in heat transfer modeling and volatile diffusion prediction within packed-bed or fluidized-bed pyrolysis reactors.

6 Conclusions

This study successfully evaluated the pyrolysis kinetics of a rice husk and corncob mixture, focusing on the main degradation stage related to bio-oil production. Using thermogravimetric analysis (TGA) at multiple heating rates, activation energy (Ea) was calculated using the KAS, FWO, and Coats-Redfern methods. The resulting Ea values ranged from 147 to 200 kJ/mol, with strong agreement between the isoconversional and model-fitting approaches. The 3D diffusion model was identified as the dominant reaction mechanism, indicating that mass transfer limitations play a key role in the thermal degradation process of the biomass mixture.

By providing validated kinetic parameters and revealing the underlying reaction mechanism, this work contributes novel insights into the thermal behavior of a rarely studied biomass mixture. The identification of the Diffusion 3D mechanism as the dominant pathway for pyrolysis of a rice husk–corncob mixture has not been previously reported, marking an important advancement in biomass co-pyrolysis studies. These findings serve as a valuable reference for optimizing reactor design—particularly for addressing mass transport limitations—and support the broader development of scalable renewable energy technologies based on agricultural waste conversion.

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Acknowledgement

The authors gratefully acknowledge the support provided by PT PLN (Persero) for this research.