



Delignification of Kelakai (*Stenochlaena palustris*) Using Sodium Hydroxide Solution: Implications on Thermal Decomposition and Kinetic Parameters

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ABSTRACT

Kelakai (*Stenochlaena palustris*) is a highly abundant wetland biomass with significant potential as a renewable energy resource. However, its high lignin content often hinders the efficiency of thermal conversion processes. This study investigated the implications of delignification using several concentrations of sodium hydroxide (NaOH) solution on thermal decomposition and kinetic parameters of kelakai. While alkali treatment is common for wood-based biomass, its specific impact on the thermal kinetics of wetland ferns remains underexplored. The objective of this research is to evaluate how reducing lignin through NaOH pretreatment enhances the quality of kelakai as a pyrolysis feedstock. Samples were treated with 3, 10, and 15% NaOH solution at 80°C under stirring at 200 rpm for 1 hour. Characterization was conducted using Thermogravimetric Analysis (TGA), and kinetic parameters were determined via the *Coats – Redfern* method. The results showed that NaOH treatment significantly shifted the lignocellulosic composition. The cellulose fraction increased from 29.64% (untreated) to 64.15% with 15% NaOH solution. Meanwhile, lignin decreased from 33.23% to 5.18% with 15% NaOH solution. TGA profiles indicated that delignified samples decomposed at a higher temperature range (245 – 380°C) with a highly significant reduction in char residue, indicating more efficient volatile conversion. Kinetic analysis demonstrated that activation energy increased from 20.42 kJ/mol (untreated) to 44.90 kJ/mol at 3% NaOH, followed by a slight decrease at higher concentrations. This behavior suggests that moderate delignification enhances cellulose structural organization and thermal stability, whereas excessive alkali treatment leads to partial cellulose degradation. These findings indicate that moderate NaOH delignification improves the thermal stability and kinetic behavior of kelakai, making it a promising feedstock for pyrolysis-based bioenergy applications.

Keywords: activation energy, kelakai, kinetic, NaOH solution treatment, thermal stability.

1. INTRODUCTION

The rising global energy demand has resulted in the depletion of non-renewable energy resources, particularly fossil fuels. Therefore, the development of renewable and alternative energy sources is considered an effective strategy to overcome the diminishing availability of conventional energy resources [1]. This condition encourages the exploration of renewable energy sources to ensure long-term energy sustainability [2]. Biomass has emerged as a promising feedstock due to its abundance, carbon-neutral properties, and potential for conversion into valuable products. Among thermochemical conversion technologies, pyrolysis is an attractive method that

converts biomass into char, non-condensable gases, and bio-oil. Bio-oil is considered a promising alternative to fossil-derived fuels and can be upgraded into higher-value fuels and chemicals [3]. One underutilized biomass source is *Stenochlaena palustris*, a native fern that grows extensively in Kalimantan peatlands and is locally known as kelakai. So far, kelakai has not been utilized optimally [4]. Chemically, the lignocellulose of kelakai presents a significant technical challenge for thermal conversion. It contains 13.8% of hemicellulose, 27.1% of cellulose, and exceptionally high lignin content of 32.11% [5]. As shown in Table 1, this lignin concentration is substantially higher than that of other common biomass

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residues, such as *Arundo donax* (9.69%) [6] or corn stover (15.91%) [7], which suggests that *kelakai* possesses a more rigid and recalcitrant structural matrix. *Kelakai* grows rapidly in peat soils and is often left unmanaged during the dry season, contributing to peatland fires that release greenhouse gases [8]. Utilizing *kelakai* for bioenergy would not only reduce this environmental hazard but also transform an abundant biomass into a valuable renewable resource, supporting local economies and advancing Indonesia's bioenergy goals [9].

Lignin is a highly recalcitrant aromatic polymer that provides mechanical strength to plant cell walls but resists thermal decomposition [10]. Its presence significantly increases the thermal stability of biomass, causing pyrolysis to require higher decomposition temperatures ($>500^{\circ}\text{C}$) for lignin breakdown, so elevated pyrolysis temperatures not only increase energy requirements but may also promote secondary cracking reactions, reducing bio-oil yield and altering its chemical composition [11].

The delignification method can be done with physical, chemical, and biological methods. But chemical treatment reduces lignin more effectively. Chemical delignification decreases lignin content by up to 35% in sengon wood and 29% in palm leaf fronds, while physical and biological methods only reduce lignin by about 17–21% and 5–6.5%, respectively [12]. Therefore, delignification using NaOH solution is one of the most widely applied methods due to its ability to cleave ether and ester linkages in lignin, solubilizing it and improving cellulose and hemicellulose access [13]. The superiority of alkali pretreatment over other methods is summarized in Table 1, where NaOH has demonstrated higher lignin removal efficiency, which is over 84% compared to acid solution or oxidative treatments in various biomass type. Furthermore, research on the impact of NaOH concentration (Table 2) shows varying effectiveness. Previous data on corn stover indicates that increasing concentration from 2.5% to 10% yields

diminishing returns in lignin reduction. However, since *kelakai* possesses a much higher initial lignin content (32.11%) [5] than common biomass, it remains unclear if higher intensities are required.

Therefore, this study investigates the effects of 3, 10, and 15% NaOH concentrations to determine the optimal threshold for *kelakai* delignification. Following treatment, it is critical to examine the thermal degradation behavior of biomass using thermogravimetric analysis (TGA) to determine weight loss trends and decomposition stages. In addition, kinetic modeling provides deeper insights into the energy requirements of each decomposition step. The Coats–Redfern method is widely employed to calculate activation energy (E) and reaction order, which are critical parameters for predicting reaction rates and optimizing reactor design and pyrolysis conditions [14].

2. RESEARCH METHODS

2.1. Materials

Kelakai was obtained from wetlands in Landasan Ulin, Banjarbaru, South Kalimantan. All parts of the *kelakai* were used in this research. *Kelakai* was dried for 48 hours to remove moisture and then sieved to pass an 18-*mesh* sieve. To further ensure the removal of water content, the raw material was dried at 60°C for 60 minutes. Sodium hydroxide (NaOH) was obtained from Sigma-Aldrich, and distilled water was used. The raw material sample (KU) was analyzed for lignocellulosic composition and thermogravimetric analysis to evaluate its thermal degradation behavior.

2.2. NaOH Solution Treatment

The dry powder of *kelakai* (KU) was mixed in 3, 10, and 15% NaOH solution (1:10 w/v) [7,10], and stirred at 200 rpm for 1 hour at 80°C to remove lignin. The samples were rinsed with distilled water until neutral pH, then dried at 60°C for 24 hours. The biomass samples obtained by NaOH solution treatment were designated as KD3, KD10, and KD15, for treated samples with 3, 10, and 15% NaOH solution, respectively.

Table 1. Comparison effect of various chemical pretreatment to lignin content.

Biomass	Pretreatment	Lignin content (%)		Lignin removal (%)	Source
		Before delignification	After delignification		
Arundo Donax	NaOH solution	9.69	1.54	84.10	[6]
Poplar wood	HCl solution	25.27	21.6	14.52	[13]
Corn stover	H ₂ O ₂ solution	15.91	3.25	79.57	[7]

Table 2. Effect of various NaOH concentrations to lignocellulosic content [7].

Biomass	Components	Untreated (%)	NaOH delignification (%)			
			2.5	5	7.5	10
Corn stover	Hemicellulose	26.92	26.68	26.01	26.81	27.20
	Cellulose	35.01	51.86	52.65	52.27	52.47
	Lignin	15.91	3.25	3.08	2.69	1.99

The samples KD3, KD10, and KD15 were analyzed for lignocellulose content and thermogravimetric analysis to evaluate the thermal degradation behavior.

2.3. Characteristics of Biomass

2.3.1. Lignocellulosic Content Analysis

The lignocellulosic composition (hemicellulose, cellulose, and lignin) of the samples was determined quantitatively using the Chesson – Data method. The procedure was carried out through a series of chemical reflux and filtration steps as follows [15]:

Step 1. Hot water soluble (a)

A total of 1 g of dried kelakai powder (constant weight) was added to 150 mL of distilled water and refluxed at 100°C for 2 hours. The mixture was filtered and washed with distilled water until the filtrate reached a volume of 300 mL and a neutral pH of 7. The solid residue was oven dried at 80°C until it reached a constant weight, named a residue (a).

Step 2. Hemicellulose Determination (b)

Residue (a) was placed into a three-neck flask with 150 mL of 0.5 M H₂SO₄ and refluxed at 100°C for 2 hours. The remaining residue was filtered, washed to pH 7, and dried to a constant weight, named as residue (b). The weight loss from this step represents the hemicellulose content.

Step 3. Cellulose and Lignin Determination (c & d)

Residue (b) was soaked in 10 mL of 72% (v/v) H₂SO₄ for 4 hours at room temperature.

The solution was then diluted with 150 mL of 0.5 M H₂SO₄ and refluxed again at 100°C for 2 hours. The final residue was filtered, washed to pH 7, and dried to a constant weight, named as residue (c). The weight loss in this step represents the cellulose content while the final remaining residue is identified as lignin (d).

The percentage of each component was calculated using the following equations (1), (2), and (3):

$$\text{Hemicellulose (\%)} = \frac{a-b}{\text{Initial weight}} \times 100\% \quad (1)$$

$$\text{Cellulose (\%)} = \frac{b-c}{\text{Initial weight}} \times 100\% \quad (2)$$

$$\text{Lignin (\%)} = \frac{c}{\text{Initial weight}} \times 100\% \quad (3)$$

2.3.2. Thermogravimetri Analysis

Thermogravimetric experiments were performed using a SEIKO TG/DTA 7300 thermogravimetric analyzer. This analysis was employed to investigate the thermal decomposition of the materials before and during NaOH treatment. Each 1 mg sample was placed in an alumina pan and heated from room temperature to 800°C at a heating rate of 10°C per minute. The nitrogen flow rate was 50 mL/min throughout the

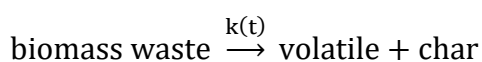
experiment. Data from each sample were collected to compute the kinetic parameters. The TGA equipment continually measured weight loss as a function of temperature and time, resulting in TG and DTG curves for each sample as shown in Equation (4).

$$\text{Weight loss (\%)} = \frac{m_0 - m_t}{m_0} \times 100\% \quad (4)$$

2.4. Kinetic Study

This study adopts the first-order reaction with the Coats – Redfern model, following the methodology proposed by Postawa et al. [15]. This model was selected because it effectively correlates thermogravimetric experimental data across various biomass samples and is mathematically equivalent to the nucleation mechanism occurring during both the initial and final stages of the pyrolysis process.

Where the Coats-Redfern method linearizes the Arrhenius equation of a non-isothermal reaction.



Where k represents the rate constant, the volatile mean of condensable (tar) and non-condensable gases. The rate constant (k) depends on the absolute temperature (T).

This is represented by the Arrhenius equation:

The kinetic equation for this system can be written as in Equation (5) [16].

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (5)$$

Where, $\frac{d\alpha}{dt}$ represents The rate of degradation. It is a linear function of temperature with a temperature-dependent rate constant, $f(\alpha)$ is the temperature a dependent function of conversion, which depends on the reaction mechanism.

The decomposition conversion (α) was shown in Equation (6).

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (6)$$

Where m_0 is the initial mass of the material, m_t is the mass of the material at time (t), and m_∞ is the final mass or residue weight of the material after degradation.

The $k(T)$ is rate constant and expressed by the Arrhenius equation in Equation (7) [14].

$$k(T) = Ae^{\frac{-E}{RT}} \quad (7)$$

By substituting Equation (5) and Equation (7) [17].

$$\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}} f(\alpha) \quad (8)$$

In the non-isothermal conversion process, TGA analysis is performed at a constant heating rate ($\beta = dT/dt$). This results in the following conversion, Equation (9) below.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} Ae^{\frac{-E}{RT}} f(\alpha) \quad (9)$$

From Equation (8) and Equation (9), the following integral is expressed by Equation (10).

$$g(\alpha) = \int_0^\alpha \left(\frac{d\alpha}{f(\alpha)} \right) = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-Ea}{RT}\right) \cdot dt \quad (10)$$

From this formula, the Coats-Redfern method was obtained to find the activation energy (E) and pre-exponential factor (A) values based on TGA data, as shown by the following Equation (11) [14,15].

$$\ln \left[\frac{g(\alpha)}{T^2 (K)} \right] = \ln \left\{ \frac{AR}{\beta Ea} \right\} \left(1 - \frac{2RT}{Ea} \right) - \frac{Ea}{RT} \quad (11)$$

Assuming, $\frac{2RT}{Ea} < 1$ [19], calculations using the following Equation (12).

$$\ln \left[\frac{g(\alpha)}{T^2 (K)} \right] = \ln \left\{ \frac{AR}{\beta Ea} \right\} - \frac{Ea}{RT} \quad (12)$$

In Equation (9), $y = \ln \left[\frac{g(\alpha)}{T^2 (K)} \right]$ vs. $= \frac{1}{T}$ are plotted. The slope of the obtained linear graphs gives $\frac{E_a}{RT}$ and the intercept gives $\ln \left\{ \frac{AR}{\beta E_a} \right\}$ activation energy (E), and the pre-exponential factor (A) can be calculated from these values. The α and T values in these equations are obtained from the TG analysis [17].

3. RESULTS AND DISCUSSION

3.1. Effect of NaOH Solution Treatment on Lignocellulose Composition

NaOH solution treatment significantly influenced the chemical composition of kelakai. The content of lignocellulose after NaOH treatment using Chesson – Data Method is shown in Table 3. Treatment at lower concentrations (KD3) resulted in a desirable decrease in hemicellulose content to 12.75%. This aligns with findings that lower NaOH concentrations induce saponification reactions between NaOH and ester bonds, thus promoting the dissolution of hemicellulose from the lignocellulosic matrix [20]. Conversely, higher NaOH concentrations (KD10 and KD15) led to an unexpected increase in the residual hemicellulose content to 17.30% and 18.80%. This phenomenon is due to the enhanced depolymerization and effective removal of lignin [21], thereby exposing and making the remaining hemicellulose fraction within the solid residue more detectable [22]. NaOH treatment significantly increases the cellulose content of kelakai, which increases from 29.64% in the untreated sample (KU) to 57.49%, 60.67%, and 64.15% for KD3, KD10, and KD15, respectively. The increase confirms the high efficacy of the delignification process in concentrating the cellulose fraction, a critical step for subsequent bio-oil production.

The results show a highly successful delignification of kelakai, with the lignin content significantly decreasing from 33.23% in the untreated sample (KU) to 21.77%, 9.41%, and 5.18% for KD3, KD10, and KD15, respectively. The study of Tsegaye et al. [23] on wheat straw showed lignin content decreasing from 17.83% to 4.36–11.28% under optimal alkaline concentrations. Similarly, delignification of *A. Donax* reduced lignin content from 9.69% to an optimal 1.54% at 5% NaOH [6]. Furthermore, research demonstrates that increasing NaOH concentrations from 14–20% intensified the chemical action, resulting in lignin removal increasing from 51.8 to 61.5% [23].

The delignification performance achieved in this work was further validated by comparing it with other studies with 3% NaOH solution, as presented in Table 4. The lignin removal efficiency of 34.48% achieved in this study is slightly lower than the 66% reported by Saynik et al. [6] and Tsegaye et al. [23] for different biomass types. This discrepancy is attributed to the higher recalcitrance of the kelakai lignocellulosic matrix, which may possess more robust lignin carbohydrate complexes (LCC).

At higher NaOH concentrations (10 and 15%), the lignin removal efficiency significantly increased to 70.69% and 83.87%, respectively. Indicating that more aggressive chemical loading can further deconstruct the biomass matrix. However, 34.48% reduction is considered sufficient to significantly enhance the pore structure of the biomass, facilitating more efficient thermal decomposition during the subsequent pyrolysis process as evidenced by the TG/DTG curves. Therefore, the lower concentrations remain the more favorable option in terms of balancing delignification effectiveness with chemical economy.

Table 3. Lignocellulosic components of kelakai after NaOH solution treatment.

Lignocellulose Analysis (wt%, dry basis)	Sample			
	KU	KD3	KD10	KD15
Hemicellulose	12.13	12.75	17.30	18.80
Cellulose	29.64	57.49	60.67	64.15
Lignin	33.23	21.77	9.41	5.18

Table 4. Comparison of lignin removal efficiency using NaOH pretreatment between this study and previous literatures.

Biomass	NaOH concentrations (%)	Initial lignin content (%)	Final lignin content (%)	Lignin removal (%)	Source
Kelakai	3	33.23	21.77	34.48	This study
	10		9.41	70.69	
	15		5.18	83.87	
Arundo donax	3	9.69	3.60	62.84	[6]
Wheat straw	3	21.03	7.10	66.09	[23]

3.2. Thermal Decomposition Behavior (TG/DTG Analysis)

The TG curves in Figure 1 illustrate the mass loss profiles of the kelakai samples due to thermal decomposition, which occurs three primary stages. This mass reduction represents the sequential degradation of the biomass constituent as shown in Table 5. The thermal decomposition of kelakai samples proceeds three distinct stages. Stage 1 (25 – 170°C) involves dehydration through the evaporation of free and bound water. Stage 2 (250–380°C) is the primary devolatilization zone, characterized by the rapid degradation of hemicellulose followed by cellulose. Stage 3 (500–800°C) represents the char formation zone, dominated by the slow decomposition of the complex lignin structure, leaving behind stable carbonaceous residue [18]. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for raw and delignified samples treated with 3%, 10% and 15% NaOH solutions are presented in Figures 1 and 2.

The dehydration stage refers to the elimination of moisture and extractive

components, occurring between 25–250°C. During this phase, water evaporation and the initial release of light volatiles take place [24]. The total mass loss recorded for KU, KD3, KD10, and KD15 was 10.17%, 12.17%, 13.08%, and 12.39%, respectively. The initial degradation temperature was observed at 179.26°C for KU, while the delignified samples KD3, KD10, and KD15 began decomposing later at 248.85°C, 247.56°C, and 245.40°C, respectively. These results indicate that NaOH treatment shifts the onset temperature to higher values at moderate concentrations (KD3), while excessive NaOH (KD10 and KD15) leads to a slight decrease. This temperature shift suggests that delignification enhances the thermal stability of kelakai biomass by removing low-stability fractions such as hemicellulose, lignin, and extractives, delaying the onset of decomposition. The untreated sample (KU) exhibited an earlier mass loss due to the presence of amorphous hemicellulose and lignin, which decompose more easily at lower temperatures [25].

Table 5. Changes in initial and final temperature during the three pyrolysis stages (dehydration, devolatilization, and char formation) for each sample.

Sample	Degradation Stages	Initial temp. (°C)	Final temp. (°C)	Mass loss (%)	Residue (%)	Peak temp. (°C)
KU	Stage 1: dehydration	25.17	179.26	10.17	24.23	316.80
	Stage 2: devolatilization	179.26	397.56	53.17		
	Stage 3: char formation	397.56	804.48	75.97		
KD3	Stage 1: dehydration	25.80	248.85	12.17	8.71	322.11
	Stage 2: devolatilization	248.85	381.63	65.52		
	Stage 3: char formation	381.63	804.63	90.77		
KD10	Stage 1: dehydration	24.43	247.56	13.08	7.37	320.04
	Stage 2: devolatilization	247.56	379.46	64.57		
	Stage 3: char formation	379.46	804.95	92.54		
KD15	Stage 1: dehydration	27.36	245.40	12.39	6.45	319.23
	Stage 2: devolatilization	245.40	378.84	64.23		
	Stage 3: char formation	378.84	804.86	93.50		

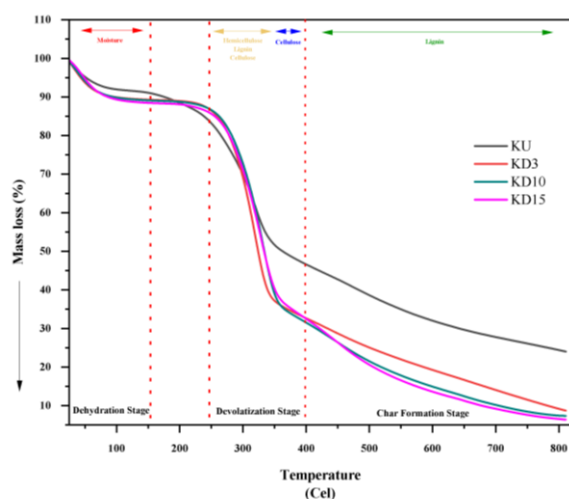


Figure 1. Thermogravimetric (TG) curves of kelakai at different concentrations of NaOH.

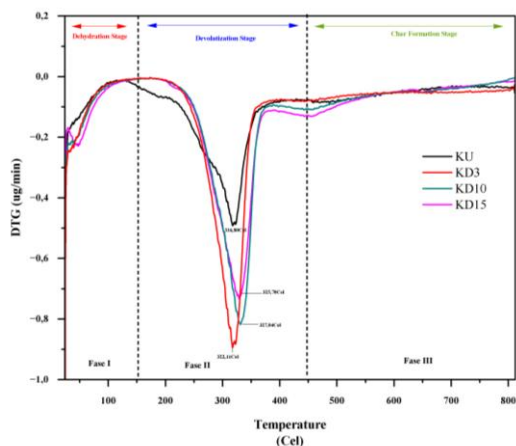


Figure 2. Derivative thermogravimetric (DTG) curves of kelakai at different concentration of NaOH.

In contrast, the predominance of crystalline cellulose in delignified samples requires higher energy to initiate degradation. A similar effect was reported by Chen et al. [26] who noted that removing thermally unstable components through alkali treatment delays initial decomposition and enhances overall thermal stability. Moreover, that alkali treatment enhances the thermal resistance of lignocellulosic materials by increasing the proportion of heat-resistant cellulose, resulting in a higher onset temperature [23,24]. However, excessive alkali concentrations may cause fibrillation, ultimately lowering the onset temperature and stability [27]. This two-fold effect demonstrates that moderate delignification improves biomass stability, whereas over-treatment deteriorates fiber structure and reduces thermal endurance. Consistent with Ait-Abdellah et al. [28], the increase in overall mass loss with higher alkali concentrations can be linked to intensified decomposition of soluble fractions.

The devolatilization step demonstrated the most substantial thermal degradation and release of volatile materials, indicating the biomass's active pyrolysis zone. As demonstrated in Table 3, this stage occurred within the temperature range of 250–380°C, corresponding to the disintegration of cellulose and minimal degradation of lignin

[17]. The untreated sample (KU) experienced a mass loss of 53.17%, while delignified samples KD3, KD10, and KD15 recorded 65.52%, 64.57%, and 64.23%, respectively. These results are consistent with Yiga et al. [29], who reported that the devolatilization phase generally involves a 50–60% mass reduction, with DTG peak temperatures near 300°C. The peak decomposition temperature ($T_{\max}$) shifted from 397.56°C for KU to 381.63°C, 379.46°C, and 378.84°C for KD3, KD10, and KD15, respectively. As shown in Figure 1, the downward shift and earlier decomposition of KD10 and KD15 compared to KD3 indicate a reduction in thermal stability. Although lignin removal was more pronounced in KD10 and KD15, excessive delignification may have partially degraded the cellulose structure and reduced the sample's thermal resistance. It simultaneously induced structural fragmentation and deterioration of the cellulose matrix. This over-treatment likely caused fiber swelling and weakened the intermolecular hydrogen bonds [33], making the cellulose more susceptible to thermal breakdown at lower temperatures than the moderately treated KD3 sample. The upward shift from KU to KD3 indicates improved thermal stability after moderate delignification, while the subsequent decline at higher NaOH concentrations suggests structural weakening due to overexposure to NaOH. The DTG curves (Figure 2) reveal that the first peak corresponds to hemicellulose degradation and the second to cellulose decomposition. The peak temperatures were 316.8°C (KU), 322.11°C (KD3), 320.04°C (KD10), and 319.23°C (KD15), with KD3 showing the highest decomposition temperature, indicating the greatest thermal resistance. The slight decrease in $T_{\max}$ at KD10 and KD15 implies that excessive NaOH concentrations (10–15%) cause fiber damage, which collectively lowers thermal stability [30]. Similar results were observed from Ebissa et al. [31], who reported that moderate NaOH treatment increased $T_{\max}$ from 355°C to 368°C, removing amorphous fractions, whereas

higher concentrations led to a decrease due to cellulose degradation. In summary, the impact of alkali treatment on thermal stability is bidirectional. At low concentrations, NaOH increases thermal stability by eliminating amorphous hemicellulose and lignin fractions. However, at higher concentrations, over delignification causes structural deterioration and fibril swelling, resulting in reduced $T_{\max}$ and overall thermal stability of kelakai biomass.

The third stage, known as the char formation or lignin combustion stage, occurs at temperatures of 500–800°C, focusing on the solid residue remaining after biomass decomposition. In this phase, the overall decomposition of kelakai biomass reached 75.97% for the untreated sample (KU), while delignified samples KD3, KD10, and KD15 showed higher decomposition levels of 90.77%, 92.54%, and 93.50%, respectively. The residual char decreased progressively with increasing NaOH concentrations, from 24.23% (KU) to 8.71%, 7.34%, and 6.35% for KD3, KD10, and KD15, respectively. These results indicate that higher NaOH concentrations promote more complete decomposition of the biomass components, reaching the optimum temperature range for lignin degradation [32]. The observed reduction in residual char correlates with the lower lignin content in delignified samples, as lignin is the most thermally stable component that contributes to char yield. This pattern supports the present TGA findings, showing that decreasing lignin content enhances the volatile fraction released during pyrolysis, thus reducing solid residue formation. Specifically, the significantly lower tail of the TG curves for KD samples in Figure 1 correlates with the drastic reduction of lignin to 5.18% (Table 3). Since lignin is the most thermally stable component responsible for char, its removal through the methodology described previously facilitates a more complete devolatilization, resulting in the minimal residual char observed. The study from Tsegaye et al. [33], reported that treatment with 3% NaOH removed 67.13% of lignin,

while 7% NaOH achieved 71.29% removal, accompanied by partial dissolution of hemicellulose by 13.77% and 26.34%, respectively.

3.3. Kinetic Analysis

Kinetic modeling is essential for understanding the thermal degradation behavior of biomass during pyrolysis [10]. The Coats-Redfern method was used in this study to conduct kinetic analysis under the assumption of first-order reaction kinetics [34]. The activation energy (E) and pre-exponential factor (A) were estimated using thermogravimetric analysis (TGA) data. The temperature range used for activation energy (E) calculation corresponded to the devolatilization stage of each sample. The calculations were performed over the devolatilization temperature range, which represents the active pyrolysis zone where the major mass loss occurs: 179.26–397.56°C (KU), 248.85–381.63°C (KD3), 247.56–379.46°C (KD10), and 245.40–378.84°C (KD15), equivalent to the degradation of cellulose and the partial breakdown of lignin [35]. The kinetic model based on the Coats-Redfern approach for the untreated sample (KU) and the delignified samples (KD3, KD10, and KD15) is presented in Figure 2.

The Coats-Redfern first-order reaction model, expressed as $\ln [g(\alpha)/T^2]$ vs. $1/T$, was applied to determine the kinetic parameters of the thermal degradation process. As shown in Figure 3, the correlation coefficients (R^2) for KU, KD3, KD10, and KD15 were 0.93, 0.98, 0.96, and 0.98, respectively, indicating an excellent linear fit. The activation energies (E)s obtained for KU, KD3, KD10, and KD15 were 20.42, 44.90, 44.64, and 40.52 kJ/mol, respectively, while the pre-exponential factors (A) were 0.048 s^{-1} , 14 s^{-1} , 12.37 s^{-1} , and 4.68 s^{-1} , respectively. The reduction in activation energy from 44.90 kJ/mol (KD3) to 40.52 kJ/mol (KD15) confirm the loss of thermal resistance due to excessive delignification. The fragmentation of the cellulose framework reduced the energy barrier required to initiate

decomposition, as the damaged structural integrity offered less resistance to heat compared to the intact cellulose crystalline matrix in KD3 [32]. The kinetic data for all samples obtained using the Coats-Redfern method are summarized in Table 6.

Table 6. Kinetic parameters for each sample at different NaOH concentrations using the Coats-Redfern methods.

Sample	E (kJ/mol)	A (s^{-1})
KU	20.42	0.048
KD3	44.90	14
KD10	44.64	12.37
KD15	40.52	4.68

The activation energy (E) of delignified kelakai samples (KD3–KD15) was markedly higher than that of the untreated biomass (KU), confirming that NaOH treatment enhanced the structural stability and resistance of the material toward thermal decomposition. The E value increased from 20.42 kJ/mol (KU) to 44.90 kJ/mol (KD3) at a maximum value, followed by a decrease at higher NaOH concentrations, which is 44.64 kJ/mol for KD10 and 40.52 kJ/mol for KD15. A similar pattern has been reported by Zhang et al. [36], who observed that delignification of corn stover using NaOH (0.5–4%) increased E value from 60.8 to 72 kJ/mol, indicating that moderate alkali exposure improves the molecular organization and bonding strength within the lignocellulosic matrix. The higher E value at 3% NaOH (KD3) suggests that partial removal of lignin and hemicellulose increases the integrity of the cellulose framework. The elimination of these thermally unstable components allows a tighter and more compact arrangement of cellulose fibrils, requiring greater energy input for the onset of degradation [37]. This structural reinforcement is reflected by the upward shift of the main DTG peak (T_{max}) at moderate concentrations, indicating delayed decomposition.

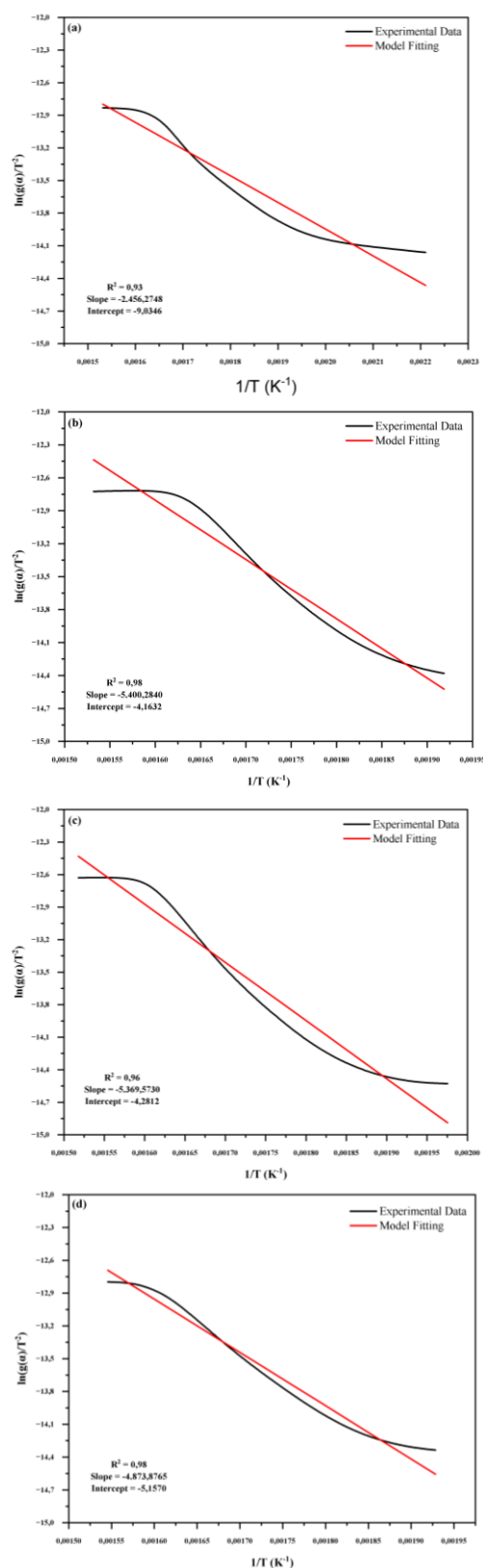


Figure 3. Kinetic parameters using coats-redfern models with first-order reaction for (a) KU, (b) KD3, (c) KD10, and (d) KD15.

However, further increases in NaOH concentrations (KD10 and KD15) lead to a

decline in E value, which implies that over-delignification causes excessive fiber swelling and depolymerization. These effects weaken intermolecular hydrogen bonding and reduce the energy barrier for thermal degradation [35]. While the removal lignin generally enhances the relative cellulose content, excessive alkali concentration can trigger over fibrillation and reduction in crystallinity. Furthermore, the transformation of cellulose I to cellulose II may compromise the structural integrity, leading to a decline in thermal stability [34]. This is evidenced by a downward shift in the onset temperature and a reduction in the activation energy required for degradation. The broader DTG peaks observed in these samples confirm that decomposition occurs more gradually due to structural disintegration and higher amorphous content. Additionally, the reduction in char residue at higher alkali concentrations reflects the more complete removal of lignin and inorganic matters, leading to a lower ash content and improved pyrolytic efficiency [36,37]. These results collectively demonstrate that alkali treatment significantly modifies the structural characteristics of kelakai biomass, enhancing its reactivity and stability during thermal conversion.

4. CONCLUSION

This study demonstrates that 3% NaOH delignification (KD3) is the optimal pretreatment condition for enhancing the pyrolysis characteristics of kelakai. This mild treatment successfully reconfigured the biomass matrix by increasing the cellulose content to 57.49% while effectively reducing lignin and hemicellulose to 21.77% and 12.75%, respectively. This compositional shift was achieved without compromising the structural integrity of the cellulose.

The thermal analysis further confirms the superiority of the 3% NaOH sample, which exhibited the highest devolatilization performance with a mass loss of 65.52%. Furthermore, the sample with 3% NaOH showed enhanced thermal stability, characterized by the highest peak

temperature (322.11°C) and the highest activation energy (44.90 kJ/mol). These results indicate that the sample with 3% NaOH provides the most favorable balance between effective delignification and thermal resistance. Consequently, 3% NaOH pretreatment is identified as the most efficient and stable condition for optimizing kelakai for pyrolysis applications.

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AUTHOR CONTRIBUTIONS

K.A.: Writing – original draft, methodology, investigation. **H.W.:** Conceptualization, writing – original draft – review & editing, methodology, resources. **A.T.:** Writing – review & editing, conceptualization, formal analysis. **I.F.N.:** Writing – review & editing, conceptualization, project administration.

CONFLICTS OF INTEREST

The authors declare no competing financial interests.

DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES

The authors declare that no generative AI or AI-assisted technologies were used in the preparation of this manuscript.

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