KINETICS AND THERMODYNAMIC ASSESSMENT OF RICE HUSK IN AN INERT ATMOSPHERE AS A FEEDSTOCK FOR ALTERNATIVE FUEL PRODUCTION

S. Umar¹, A.A. Yakatun¹, I.Y. Mohammed², E.M. Ezeh³, Y.A. Abakr⁴

¹Department of Chemical Engineering Federal Polytechnic P.M.B 55 Bida, Niger State, Nigeria.
²Department of Chemical Engineering Abubakar Tafawa Balewa University Bauchi, 740102 Nigeria
³Department of Chemical Engineering, Federal University Otuoke Bayelsa, Nigeria
⁴Department of Department of Mechanical, Materials and Manufacturing Engineering, University of Nottingham Malaysia, Jalan Broga, Semenyih 43500, Selangor Darul Eshan, Malaysia

Abstract

The utilisation of rice husk as a feedstock for alternative fuel production is an area of growing interest due to its abundance and potential as a renewable energy source. This study reports investigation of kinetics and thermodynamics of rice husk pyrolysis in an inert atmosphere. Experimental analysis, including proximate, ultimate structural composition and thermogravimetric analyses (TGA), were conducted to determine the proximal, ultanal, chemical composition and pyrolysis characteristics of rice husk under inert conditions. Kinetics of the pyrolysis process was evaluated using distributed activation energy model (DAEM) while thermodynamic parameters such as activation energy ($E_A$), changes in enthalpy ($\Delta H$), entropy ($\Delta S$), and Gibbs free energy ($\Delta G$) were computed to provide insights into the reaction mechanisms. The feedstock exhibited ash content, fixed carbon, volatile matter, and higher heating value on dry basis of 13.56 wt%, 16.37 wt%, 70.07 wt% and 15.22 MJ/kg respectively while the result of ultimate analysis showed carbon, hydrogen, nitrogen, sulphur and oxygen content of 40.95, 5.67, 0.22, 0.09 and 52.17 wt%. The chemical composition result (water extractives-free) indicated cellulose, hemicelllos and lignin content of 39.12, 17.56 and 22.43 wt%. The kinetics analysis revealed that the pyrolysis process followed a single-order reaction mechanism and irreversible, suggesting that the pyrolysis reactions proceed in a direction that favors the formation of products. The average $E_A$, $\Delta H$, $\Delta S$ and $\Delta G$ required for the pyrolysis reactions was established to be 140.56 kJ/mol, 137.00 kJ/mol, -135.25 J/mol and 222.38 kJ/mol respectively. The comprehensive assessment of the feedstock affirms its suitability for alternative fuel production towards a greener energy landscape.

Keywords: Rice husk, proxanal, ultanal, kinetics, thermodynamics, pyrolysis

1.0 INTRODUCTION

Currently, fossil fuels dominate the global energy landscape and are anticipated to remain so for the foreseeable future. Despite growing concerns regarding greenhouse gas emissions and their environmental impact, effective solutions remain elusive. While technologies like enhanced fossil fuel conversion and carbon capture and storage exist, they are prohibitively expensive. Consequently, there is a burgeoning interest in transitioning to low-carbon alternatives such as biomass. Biomass is hailed as a carbon-neutral solution to climate change, capable of being converted into various energy precursors to foster sustainable production methods. With the United Nations advocating for limiting global temperature rise to below 2°C, sustainable agricultural practices have emerged as a pivotal strategy (Mohammed et al., 2023; Mohammed et al., 2017a). The recent agricultural transformation policy implemented by the Nigerian government has sparked a notable surge in rice cultivation nationwide. This strategic initiative has not only incentivized but also facilitated the establishment of
numerous modern rice mills across various regions of the country. These mills, ranging from small to large-scale operations, play a pivotal role in streamlining the processing of paddy rice into finished products (Salisu et al., 2021). Rice husk, a residue from rice milling operation, seemed to be highly underutilised rarely integrated into processing as either source energy or processed into valuable products. This waste stream constitutes an additional waste management challenge with open burning as the major source of disposals (Achebea & Nwanya, 2021). In the region of Niger State, particularly in Bida and its environs, rice husk stands out as a valuable but often neglected resource. Despite its abundant presence, this lignocellulosic material has not received the attention it deserves as a potential biofuel feedstock. By harnessing the latent energy within rice husk through thermochemical conversion process could unlock a new avenue for clean and renewable energy production. This will not only reduce greenhouse gas emissions but also creates opportunities for job creation, rural development, and energy security. The objective of this study was to conduct a comprehensive assessment of rice husk in order to understand its profile and transformation characteristics.

2.0 MATERIALS AND METHODS

2.1. Raw materials
Rice husk sample was collected from Bida rice mill in Niger State. The sample collection was done manually from various layers of the material, including the top, middle, and bottom, in an alternating fashion. To mitigate potential decomposition by micro-organisms, the initially high-moisture samples were sun pre-dried, following the guidelines of BS EN 15442:2011. Subsequently, the material was ground to particle sizes ranging from 0.2 mm to 2 mm and stored in airtight plastic bags for subsequent investigations. The proximate analysis on dry basis such as fixed carbon, volatiles, and ash content of the sample were conducted according to the procedure outlined in Mohammed et al. (2022). The ultimate analysis was conducted using a TRUSPECHN® elemental Analyser from LECO, US. In summary, the instrument was calibrated following the guidelines outlined in the operating manual for CHN analysis. Calibration samples, enclosed in tin aluminium foil cups (LECO®), were sealed, and fired at 950 °C in an ultra-high pure oxygen atmosphere (99.993% purity) using helium as a carrier gas for combustion products. This procedure was applied to approximately 0.15 g of dried biomass sample, and the experiment was replicated in triplicates for reproducibility. The oxygen (O) mass fraction was determined by the principle of difference. The structural analysis of the biomass was determined following the prescribed procedure in the National Renewable Energy Laboratory Technical Report NREL/TP-510-42618. Ash mineral composition was assessed using scanning electron microscopy, SEM-EDX (FEI Quanta 400 FE-SEM, Hillsboro, OR, USA). The ash sample was placed on the carbon tape of the sample holder and positioned in the sample compartment of the x-ray. Scanning of the sample was conducted under low vacuum and the inorganic components present in the ash were recorded. Higher heating value (HHV) was determined using oxygen bomb calorimeter Parr 6100 following BS EN 14918. Nearly 1.00-2.00g of the sample was pelletised and placed in the metal crucible. Ignition wire in a u-shape was hung on the bomb cover and positioned appropriately with the tip the wire touching the sample. The bomb cover was then fixed to the bomb container with the sample carefully arranged inside it. Subsequently, the closed bomb was pressurised with purified oxygen until the pressure reached the desired set point. The pressurised bomb was inserted in a 2.0L container with water in it and the system was closed. The bomb calorimeter was set on for the sample combustion until the process was completed. Thermogravimetric analysis (TGA) was carried out in an inert atmosphere at a flow rate of 20 mL/min. The decomposition profile was examined across a temperature range from ambient to 850 °C at heating rates of 5, 10, and
15 °C/min. The sample, with a particle size of 0.2 mm and approximately 7.0 mg in weight, was used for the investigation. During the tests, the simultaneous recording of sample weight loss and derivative weight loss concerning with respect to the temperature were recorded accordingly.

Investigation into the kinetics of thermal decomposition of lignocellulosic materials has involved the application of various models, each providing distinct insights into the complex degradation processes. Distributed activation energy model (DAEM) represents a more accurate and sophisticated approach in elucidating the thermal decomposition characteristics of solid fuels. This model surpasses its counterparts by virtue of its capacity to mathematically capture and represent the inherent physical and chemical heterogeneity exhibited by solid fuel materials. Generally, Solid fuels often comprise a heterogeneous mixture of diverse components, each with distinct physical and chemical properties. The DAEM acknowledges this complexity by introducing a distribution of activation energies, allowing it to account for the various reactions and pathways that different components within the solid fuel may undergo during thermal decomposition (Mohammed et al., 2018a; Mohammed et al., 2018b; Navarro et al., 2018; Szűcs et al., 2020; Yan et al., 2020). The DAEM is considered to be more accurate, and the insightful observation suggests that, at a consistent conversion rate denoted as V/V*, the activation energy exhibits a continuous distribution, classily represented by a function f(E). This departure from a singular activation energy value acknowledges the heterogeneous composition of the reactants and the complexity inherent in their simultaneous decomposition. In this analytical framework, all the parallel reactions are considered to be irreversible and first-order concerning the remaining volatile content. This adherence to the principles outlined by Miura and Maki (1998) establishes a robust foundation for understanding the kinetics of the reactions unfolding during thermal conversion as presented in equation (1).

\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{k_0 R}{E} \right) + 0.6075 - \left( \frac{E}{R} \right) \frac{1}{T} \tag{1}
\]

The kinetics can be established following the steps summarised below:

i. Generate a conversion-versus-temperature graph using TGA data derived from at least three distinct heating rates.

ii. Compute \((\beta/T^2)\) at specific conversions, utilizing the relationship established in step (i) for the various heating rates.

iii. Develop a graph plotting \(\ln(\beta/T^2)\) against \((1/T)\) at the chosen conversions. Calculate the activation energy and pre-exponential factor from the slope and intercept based on equation (1).

iv. Construct a graph portraying activation energy values obtained in step (iii) against the conversion. Further, differentiate the model to acquire the distribution function for activation energy.

Frequency factor, often referred to as the pre-exponential factor, is expressed as a function of activation energy, as detailed in equation (2) below. This mathematical representation serves to establish a crucial relationship between the pre-exponential factor and the activation energy.

\[
k_0 = k_1 e^{k_2 E} \tag{2}
\]

In the given expression, \(k_1\) and \(k_2\) represent constants dependent upon the specific characteristics of the reacting material. This equation can be transformed into a linearized form denoted as equation (3) and the values of \(k_1\) and \(k_2\) can be easily derived from the slope and intercept.

\[
\ln (k_0) = \ln (k_1) + k_2 E \tag{3}
\]
Thermodynamic parameters are calculated by leveraging key kinetic factors such as activation energy and frequency factor, alongside constants like Boltzmann and Planck constants. Among these thermodynamic parameters, the change in enthalpy ($\Delta H$), entropy ($\Delta S$), and Gibbs free energy ($\Delta G$) play pivotal roles in unraveling the underlying energetic transformations associated with a given reaction. According to Kim et al. (2010), these parameters can be computed using the following equations:

\[
\Delta H = E_a - RT \tag{4}
\]
\[
\Delta G = E_a + RT_m \ln \left( \frac{K_B T_m}{hA} \right) \tag{5}
\]
\[
\Delta S = \frac{\Delta H - \Delta G}{T_m} \tag{6}
\]

Where $K_B$ is the Boltzmann constant ($1.83 \times 10^{-23}$ J/K), $h$ is the Planck constant ($6.36 \times 10^{-34}$ J.s), $T_m$ is the peak temperature at maximum weight loss in the DTG curve.

### 3.0 RESULTS AND DISCUSSION

The physicochemical attributes of the rice husk biomass are summarised in Table 1. The proximate analysis results unveil the composition of rice husk sample on a dry basis, with ash content, fixed carbon, and volatile of 13.56 wt%, 16.37 wt% and 70.07 wt% respectively with the corresponding heating values of 15.22 MJ/kg. These attributes are similar to the literature values reported for a typical rice husk biomass (Fadhilah et al., 2023; Zaidi et al., 2023). The result of ultimate analysis indicated that the biomass sample exhibited 40.15 wt% carbon, 5.98 wt% hydrogen, 0.41 wt% nitrogen, 0.78 wt% sulphur and 52.68 wt% oxygen. Fadhilah et al. (2023) reported ultimate analysis of a typical rice husk sample to be 38.23 wt% carbon, 5.48 wt% hydrogen, 1.27 wt% nitrogen and 0.15 wt% sulphur, which are in good agreement with values obtained herein. Accordingly, the chemical composition analysis showed the presence of cellulose (39.12 wt%), hemicellulose (17.56 wt%), and lignin (22.43 wt%) in the sample. This characteristic provides crucial insights into the structural components of the samples.

<table>
<thead>
<tr>
<th>Property</th>
<th>Rice husk</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis (wt%)</strong></td>
<td></td>
</tr>
<tr>
<td>Ash content</td>
<td>13.56</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>16.37</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>70.07</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>15.22</td>
</tr>
<tr>
<td><strong>Ultimate analysis (wt% db)</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>40.15</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.98</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.41</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.78</td>
</tr>
<tr>
<td>Oxygen</td>
<td>52.68</td>
</tr>
<tr>
<td><strong>Chemical composition analysis (wt%)</strong></td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>39.12</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>17.56</td>
</tr>
<tr>
<td>Lignin</td>
<td>22.43</td>
</tr>
</tbody>
</table>

The elemental scanning of the ash from EDX-SEM analysis (Figure 1) pinpointed silica and potassium as the predominant inorganic minerals present within the ash, with silica emerging as the dominant component. The prominence of silica in the ash composition indicates the prevalence of silicon-rich compounds within the original sample, which holds implications for the thermal behavior, reactivity, and overall performance of the ash in different applications, particularly in the context of biofuel production (Mohammed et al., 2017b).

The thermogravimetric (TGA) characteristics of samples under nitrogen atmosphere at three different heating rates is shown in Figure 2. The process proceeded in three stages, pre-maximum degradation (I), maximum degradation (II), and post maximum...
degradation (III). biomass during storage or handling.

Stage I, under 100 °C represents initial weight loss (9.0 wt%) due to evolution of moisture, as exhibited by the sample, signifying the hydroscopic nature of the sample. This observation agrees with the fact that the biomass samples were initially dried before further processing. Furthermore, the region between 100-200 °C (pre-maximum degradation stage) exhibited no visible shoulders on the derivative thermogravimetry (DTG) for all the heating rates, which signifies that the degradation of extractives aligned substantially with that of some hemicellulose component. Studies on the thermal devolatilisation of rice husk in the literature showed comparable trend in the DTG profile (Zaidi et al., 2023). Beyond 200 °C, stage II (200-400°C), a noticeable shoulder is observed, which represent distinct degradation of hemicellulose. The overall weight loss of 43wt% was recorded under this stage. This is due to combination of decomposition of hemicellulose coupled with cellulose devolatilisation (Hierro-Iglesias et al., 2024). The reaction intensity at maximum degradation point ranged from -5.2 wt%/°C, -7.39 wt%/°C and -6.66 wt%/°C was recorded at 5, 10 and 15 °C/min. Generally, increasing heating rates result in increased reactivity due to efficient heat transfer between the individual biomass particles (Mohammed et al., 2022). However, the trend portrayed by the rice husk sample could be attributed to the level of volatile component present in the sample. This observation is in good agreement with the proxanalog attributes particularly, the volatile matter (Table 1) (Zaidi et al., 2023).

**Figure 1:** EDX-SEM of rice husk ash

![EDX-SEM of rice husk ash](image1)

**Figure 2:** Thermogravimetric profile of rice husk sample at different heating rates under 20ml/min nitrogen

![Thermogravimetric profile of rice husk sample](image2)
Stage III is the post maximum devolatilisation at temperature beyond 400 °C, which involves evolution of heavy molecular weight component particularly lignin-derived components in addition to the decomposition of char remnant from cellulose and hemicellulose (Mohammed, 2017). Under this temperature regime, the average weight loss recorded was 20.65 wt%. These characteristics strongly aligned with the proximate analysis results, particularly the lignin content of the biomass sample. Considering the DTG curves, no noticeable shoulder exhibited by the sample, suggesting the lignin component in the biomass has uniform thermal degradation.

The specifics of how the biomass sample would behave in the actual pyrolysis process with respect to temperature is shown in Figure 3. It revealed the degree of conversion of the samples spanned from 10% to 90% at different heating rates, which indicates that significant chemical changes take place within the biomass.

![Figure 3: Rice husk conversion in an inert atmosphere with respect to temperature at different heating rate](image)

The biomass sample displayed 10% conversion at 274, 225 and 219 °C for 5, 10 and 15 °C/min heating rate respectively. This temperature range represents the decomposition of hemicellulose component in the sample. The difference in the degradation temperature observed under the same conversion suggests that at low heating rate, the pyrolysis mechanism differs from that of high heating rate due to differences in heat transfer mechanism. At conversion range of 0.2-0.5 with temperature range of 290-352 °C, the biomass sample showed similar pyrolysis mechanism, suggesting that the cellulose component of rice husk have similar decomposition profile irrespective of the heating rates applied. Furthermore, at conversion between 0.6-0.9 under 350-704 °C, the pyrolysis mechanism at 10 and 15 °C/min heating rates are similar but significantly different from the process observed at 5 °C/min due to gradual decomposition of individual biomass components.

Figure 4 depicts biomass sample pyrolysis linear plot derived from ln(β/T^2) with respect to (1/T) at the selected conversions based on the equation (1). Imaginary line through the points at each of the heating rate showed a parallel relationship, indicating equal gradient and similar characteristics. A linear fit to the set of three different heating rates at the same conversion showed very good relationship between ln(β/T^2) and (1/T) with R-squared value of 0.6615-0.9840 as summerised in Table 2 with their corresponding activation energy and the pre-exponential factor computed from the slope and intercept of the linear fit.

### Table 2: Kinetic parameters of rice husk sample

<table>
<thead>
<tr>
<th>V/V*</th>
<th>E_a(kJ/mol)</th>
<th>R^2</th>
<th>k_0(s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>158.31</td>
<td>0.6615</td>
<td>1.52E+23</td>
</tr>
<tr>
<td>0.3</td>
<td>188.51</td>
<td>0.7007</td>
<td>2.45E+25</td>
</tr>
<tr>
<td>0.4</td>
<td>265.91</td>
<td>0.5881</td>
<td>4.34E+31</td>
</tr>
<tr>
<td>0.5</td>
<td>252.47</td>
<td>0.6219</td>
<td>8.07E+29</td>
</tr>
<tr>
<td>0.6</td>
<td>51.62</td>
<td>0.9084</td>
<td>1.88E+12</td>
</tr>
<tr>
<td>0.7</td>
<td>50.3</td>
<td>0.9840</td>
<td>6.44E+11</td>
</tr>
<tr>
<td>0.8</td>
<td>61.73</td>
<td>0.9551</td>
<td>1.62E+12</td>
</tr>
<tr>
<td>0.9</td>
<td>95.64</td>
<td>0.8643</td>
<td>6.63E+13</td>
</tr>
</tbody>
</table>

Average value: 140.56 | 5.53E+30
The plots showed that within 0.5 degree of conversion of the sample, the imaginary vertical lines are near-perfect parallel lines, connoting similar process phenomenon. This region is within the cellulosic (hemicellulose and cellulose) degradation, which can be inferred that the mechanisms are somewhat similar. The process generally proceeds via fast depolymerization that involve cleavage of the glycosidic bond between the monomeric units, leading to the formation of anhydrosugar and carboxylics that further undergo fragmentation and dehydration with small molecules such as water, carbon II and carbon IV oxides as some of the products (Mohammed, 2017). Furthermore, this stage seemed to be the rate limiting step as the activation energy values increased within this conversion region as well as increased pre-exponential factor (Table 2). This is not surprising due to crystalline attributes associated with cellulose, which makes it thermally stable and requires higher energy to overcome the barrier to effect any chemical transformation (Zhang et al., 2024). Beyond 0.5 degree of conversion, the level of parallelism in the imaginary vertical lines changed, suggesting different mechanism, which also tends towards the left-hand side. These observations indicate that the concentration of vertical and parallel imaginary lines at top right-hand side represent a rate limiting step during the pyrolysis while those towards the left-hand side represent mechanism with low activation energy.

The activation energy distribution of the samples with respect to the conversion is presented in Figure 5.

Accordingly, at conversion 0.2-0.5, a somewhat positive relationship is observed with corresponding change in the activation energy from 158.31 to 265.91 kJ/mol (Table 2). This change is probably due to increasing activation of molecules for chemical reaction, which may include complex reactions during devolatilisation involving multi-step mechanisms within the solid samples (Boubacar Laougé & Merdun, 2020). Subsequently, declining trends in the activation energy values were observed for all the samples at conversion beyond 0.5, probably due to decrease in the residual volatile content, particularly from the hemicellulose and cellulose contents present in the sample in addition to lignin depolymerisation, which is usually associated with low value of the activation energy due to its non-crystalline nature (Zhang et al., 2024).
Furthermore, the sample (Figure 5) exhibited activation energy distribution pattern between 0.7 and 0.9 degree of conversion, which represents residual char degradation in the pyrolysis process. The pre-exponential factor ($k_0$), which is the frequency of collisions between molecules during the pyrolysis (Table 2) showed different exponents levels of $>10^{20}$ and $<10^{15}$ at 0.2-0.5 and 0.6-0.9 degree of conversion. The lower values of $k_0$ recorded suggests low reaction barrier, low molecular collision, and easier conversion whereas the higher $k_0$ values signifies more heat requirement for higher molecular collision to be transferred and higher energy barrier to be overcome for the reaction to progress. These observations are strongly in good agreement with the observed activation energy values. According to Fong et al. (2019), $k_0$ values for a thermochemical conversion of biomass within $10^9$ is typically attributed to limitations in the rotation of the activated complex in relation to the initial reactant molecules. This limitation is indicative of a reaction mechanism dominated by surface interactions. In thermochemical processes like pyrolysis, the surface reactions are crucial, as the reactants are often solid biomass particles whose conversion depends heavily on the interactions at the material's surface with the surrounding heat and reactant gases. The restriction in rotation suggests that the activated complex, a transitional molecular structure that results from the initial collision of reactant molecules and precedes the formation of product molecules, is confined in such a way that it can only rotate to a limited extent. This confinement potentially enhances the likelihood of a successful reaction occurring at the surface of the biomass, as the complex remains oriented in a favourable position for reaction longer than it might if free rotation were possible. On the other hand, pre-exponential factor above $10^9$ indicates a scenario where the rotation of the activated complex and reactants does not undergo any significant change during the course of the reaction. This suggests that the reaction dynamics are different, possibly involving a more homogeneously distributed energy and interaction throughout the reacting materials rather than being limited to the surface. Such conditions are typical in gas-phase reactions, where molecules have the freedom to move and rotate, leading to different reaction kinetics and mechanisms compared to those dominated by surface interactions.

The relationship between $\ln k_0$ and activation energy is shown in Figure 6. This represents a linear fit that indicate compensation, suggesting for any increase in the activation energy is accompanied by an increase in the pre-exponential factor, or vice versa. This compensation effect can often mean that even though a reaction might require more energy ($E_a$) to initiate, it can still proceed at a comparable rate due to a correspondingly higher $k_0$. This is so since reactions with higher activation energies involve molecular configurations that, once achieved, allow reactants to convert to products more efficiently, thereby increasing the $k_0$. From the Figure 6, the sample exhibited positive slope, which implies that as the activation energy increased, there is corresponding increase in the value of pre-exponential factor. This is indicative of a compensation effect where higher barriers to reaction are compensated by higher frequencies of successful collisions or configurations conducive to reaction. The intercept, a point where activation energy is zero or extremely minimum. The positive high value recorded (15.59) implies high rate of reaction under minimum energy barrier, suggesting that under ideal conditions, the reaction could proceed very rapidly. Furthermore, the decomposition rate of rice husk appeared to be faster due to high value of the intercept recorded. This observation strongly agreed with the activation energy distribution pattern in the Figure 5 above. The sample exhibited relatively small area under curve, which translate to low cumulative activation energy required for the reaction to progress from initial reactants to final products across all conversion levels. The value of $k_1$ and $k_2$ obtained from the slop and intercept is $5.91 \times 10^6$ and 0.2172.
The summary of thermodynamic parameters, such as changes in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), assessed for the pyrolysis process of the biomass sample is presented in Table 3.

<table>
<thead>
<tr>
<th>V/V*</th>
<th>ΔH (kJ/mol)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔS (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>156</td>
<td>278</td>
<td>-194</td>
</tr>
<tr>
<td>0.3</td>
<td>186</td>
<td>335</td>
<td>-236</td>
</tr>
<tr>
<td>0.4</td>
<td>263</td>
<td>488</td>
<td>-356</td>
</tr>
<tr>
<td>0.5</td>
<td>250</td>
<td>454</td>
<td>-323</td>
</tr>
<tr>
<td>0.6</td>
<td>48</td>
<td>40</td>
<td>14</td>
</tr>
<tr>
<td>0.7</td>
<td>46</td>
<td>33</td>
<td>21</td>
</tr>
<tr>
<td>0.8</td>
<td>57</td>
<td>49</td>
<td>12</td>
</tr>
<tr>
<td>0.9</td>
<td>90</td>
<td>102</td>
<td>-20</td>
</tr>
</tbody>
</table>

Average value 137.00 222.38 -135.25

In this study, the recorded values ΔH showed a notable trend concerning conversion levels. Increase in the ΔH values was observed as the conversion progressed up to 0.5 conversion. Following this initial rise, a distinct decline in ΔH value occurred below 100 kJ/mol within the conversion range of 0.6 to 0.9. This trend suggests dynamic changes occurring within the pyrolysis process as conversion progresses. The initial increase in ΔH may indicate heightened energy absorption as the pyrolysis reaction advances, possibly due to factors such as improved accessibility of reactants or accelerated reaction kinetics. However, beyond a certain point, the decreasing ΔH values imply a diminishing trend in the energy changes associated with the pyrolysis process. This decline could stem from factors such as depletion of reactants, alterations in pyrolysis mechanisms, or variations in the pyrolysis environment. This is in good agreement with our earlier observation that suggested conversion of residual hemicellulose, full breakdown of cellulose and some parts of the lignin under similar conversion range. Furthermore, the pattern observed in the ΔH values mirrors that of the activation energy, albeit with a slight discrepancy of around 2.0-5.0 kJ/mol across all conversion levels (Table 3). This consistency between the changes in enthalpy and activation energy highlights the feasibility of the pyrolysis reaction. Such close correspondence suggests that the energy requirements for initiating and sustaining the pyrolysis process aligned closely with the energy changes occurring throughout the reaction. In chemical reactions, a substantial difference between the activation energy and the enthalpy change indicates a significant disparity in the energy barriers for initiating the reaction and the energy released or absorbed during the reaction. A large gap between these values often implies a less favourable or improbable reaction, as the energy needed to initiate the reaction far exceeds the energy changes driving the reaction forward. On the other hand, the small discrepancy observed in this study suggests a harmonious relationship between the activation energy and the enthalpy change, indicating that the energy required to kick-start the pyrolysis process is well-balanced with the energy changes occurring as the reaction progresses. This alignment supports the likelihood and feasibility of the pyrolysis reaction, implying that the energy barriers for initiating the process are within a reasonable range relative to the overall energy changes.
involved. The positive values of $\Delta H$ recorded implies that external heat is required to generate the activated complex during the pyrolysis (Boubacar Laougé & Merdun, 2020; Mohammed et al., 2022). The change in entropy ($\Delta S$) serves as a crucial indicator in thermodynamics, shedding light on the nature and directionality of a process. A positive change in entropy ($\Delta S > 0$) typically implies that a process is likely to proceed spontaneously, moving in a direction that increases the overall disorder or randomness of the system. This spontaneous direction is often the natural tendency of processes in isolated systems, where they evolve to maximize entropy. On the contrary, a negative entropy change ($\Delta S < 0$) indicates a decrease in disorder, suggesting that the process is less likely to occur spontaneously and may require external energy input to proceed. In such cases, the process might not move forward in the defined or expected direction; instead, it might either halt or potentially reverse, moving in a direction that leads to a more ordered state. The $\Delta S$ values obtained for the sample displayed a dynamic trend across various conversion levels. Initially, from conversion levels of 0.2 to 0.7 (Table 3), the recorded $\Delta S$ values for the sample during its pyrolysis process shifted from negative to positive across different stages of conversion. Specifically, at the conversion levels of 0.2 to 0.5, the $\Delta S$ values were negative, suggesting a phase where the system was becoming more ordered, possibly due to the formation of more structured intermediate compounds. This indicates that during these stages, the decomposition of rice husk involves a reduction in randomness or disorder, which could be attributed to the breakdown of more complex molecular structures into simpler, more ordered forms. As the conversion progressed further to levels between 0.6 and 0.8, the $\Delta S$ values transitioned to positive, reflecting an increase in disorder or randomness within the system (Zaidi et al., 2023). This change could be indicative of a phase where volatile substances are released more extensively, leading to increased randomness as different chemical species and fragments are generated. These phenomena exhibited by the sample is in good agreement with our earlier study where it was stated that lignocellulosic biomass undergo initial thermal disintegration into individual component and subsequent devolatilisation via series of parallel reactions (Mohammed et al., 2019a; Mohammed et al., 2019b). The Gibbs free energy change ($\Delta G$) serves as a comprehensive indicator of the overall energy transformation during the pyrolysis reaction. The $\Delta G$ values recorded for the rice husk sample showed a distinct segregation into two sections. Between conversion levels of 0.2 to 0.5, the $\Delta G$ values ranged from 278 to 454 kJ/mol (Table 3), indicating a higher energy requirement for the pyrolysis reaction during this phase. However, at conversion levels of 0.6 to 0.9, the $\Delta G$ values decreased substantially, ranging from 40 to 102 kJ/mol. This suggests that the pyrolysis reaction for rice husk also becomes significantly more favourable in the later stages of conversion, with lower energy requirements facilitating easier progression of the reaction. This characteristic agreed with the fact that the later degradation profile predominantly represent lignin devolatilisation which is a non-crystalline material (Zaidi et al., 2023; Zhang et al., 2024).

4. CONCLUSION

Kinetics of the pyrolysis process was evaluated using distributed activation energy model (DAEM) while thermodynamic parameters such as activation energy, enthalpy, entropy and Gibbs free energy changes were computed to provide insights into the reaction mechanisms. The feedstock displayed the following characteristics on dry basis: an ash content of 13.56wt%, indicating the inorganic mineral content present in it; a volatile matter content of 70.07wt%, signifying the proportion of combustible gases and volatile compound; a fixed carbon content of 16.37wt%, representing the solid carbonaceous residue left after volatile matter has been driven off and a higher heating value of 15.22MJ/kg, denoting the energy content per unit mass of the fuel.
The kinetics analysis revealed that the pyrolysis process follows a single-order reaction mechanism, indicating that the rate of decomposition is directly proportional to the concentration of the volatile reactants remaining in the feedstock. Furthermore, the kinetics were determined to be irreversible, suggesting that the pyrolysis reactions proceed in a direction that favors the formation of products. The average activation energy required for the pyrolysis reactions was calculated to be 140.56 kJ/mol, representing the energy threshold that must be overcome for the reaction to occur. The enthalpy change associated with the pyrolysis process was found to be 137.00 kJ/mol, reflecting the heat absorbed or released during the reaction. Furthermore, the Gibb’s free energy change, calculated to be 222.38 kJ/mol, indicates the spontaneity of the pyrolysis reactions. A negative Gibb’s free energy value suggests that the reactions are thermodynamically favorable under the given conditions, driving the conversion of the feedstock into alternative fuels. Lastly, the entropy change, recorded at -135.25 J/mol, signifies the degree of disorder associated with the pyrolysis process. The thorough evaluation of the feedstock confirms its aptness for the production of alternative fuels, contributing to the advancement of a more environmentally sustainable energy paradigm.

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