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Insights Into the Behavior and Kinetics of Purun Tikus Degradation During Slow Pyrolysis

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Abstract

Purun tikus (Elocharis dulcis), a type of wetland biomass feedstock, is a challenge to the swamp ecosystem as it contributes to pollution in the area. Hence, integrating the use of purun tikus as a source of bioenergy, particularly in the form of bio-oil, is of the highest priority. Nevertheless, there is a lack of research on the degradation rate of purun tikus conversion to bio-oil through pyrolysis. Thus, this study aims to evaluate the rate of destruction of purun tikus in the process of conversion into bio-oil via pyrolysis. In the experiment, a batch reaction vessel was used to carry out slow pyrolysis at temperatures ranging from 300 to 500 °C, and the reaction times ranged from 60 to 120 min. By assuming a first-order process and using the Arrhenius equation, it was possible to figure out the activation energy and the preexponential factort. To determine whether purun tikus destroyed during pyrolysis, an activation energy of 43.317 kJ mol^{-1} and a pre-exponential factor of 0.351 s^{-1} were identified.

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1. Introduction

Energy is widely recognized as a fundamental requirement for everyday existence (Alkul et al., 2022; Farobie and Hartulistiyoso, 2022; Haque, 2021; Osman et al., 2022; Shahinzadeh et al., 2022). Pyrolysis technology is considered a good way to produce energetic bio-oil, an oil-based fuel that can potentially replace (Amrullah et al., 2022b; Omoriyekomwan et al., 2021). Biomass is decomposed by heat at high temperatures in low oxygen or near-oxygen-free conditions, with or without catalysts. The common feedstock for the pyrolysis process used to generate bio-oil is lignocellulosic biomass (Chang, 2020; Farobie et al., 2022). This includes palm kernel shells, wood chips, rice husks, coconut fibers, and other agricultural wastes. Since these terrestrial biomasses, they compete with other industries, including the food and feed industry, for resources, including fertilizers, land, and freshwater. (Farobie et al., 2021; Greene et al., 2020; Liew et al., 2021).

Indonesia generates large amounts of agricultural waste, forestry waste, and tidal marsh plants owing to its large agricultural and forestry sectors and swamps. These resources fall under the wet

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biomass classification. Consequently, replacing Indonesia's fossil fuel supply with biomass is an innovative way secure energy and valuable chemicals for the entire nation. Rony et al. (2019), say that most lignocellulosic biomass is made up of cellulose (32–45%), lignin (14–26%), and hemicellulose (19–25%). As a result, they have the potential to be transformed into gaseous, solid, and liquid fuels, which can be employed for heat, electricity, and energy production. Biomass energy offers numerous benefits compared to conventional fossil fuels, including shorter lifecycles, broader availability, and reduced greenhouse gas emissions, as indicated by (Cheng et al., 2019)

Numerous approaches, including thermochemical, biochemical, and physicochemical conversion, convert biomass into usable energy. Thermochemical conversion is widely used because it is fast and can process various types of biomass without any limitations (Dhyani and Bhaskar, 2018). Gasification (Amrullah and Matsumura, 2019), torrefaction (Gong et al., 2016), combustion (Gurevich Messina et al., 2017), and pyrolysis (Yu et al., 2016) are viable thermochemical methods. Pyrolysis, which is conducted at 300–600 °C in an inert environment, transforms bio-oils, biogas, and coal into their respective products. Researchers have attempted to use pyrolysis to convert lignocellulosic biomass into bio-oil for use as fuel and valuable chemicals, such as phenolic compounds. Naron et al., (2019) studied different catalyst agents' effects on phenol production during the pyrolysis of lignin from hardwood, softwood, and grass plants, noting that various lignin types had distinct interactions with the catalyst.

Various biomass, including rice straw, waste tyres, sawdust, swine manure, algae, empty fruit bunches, and switchgrass, have been used to produce bio-oil through pyrolysis (Biswas et al., 2018, (Seng-eiad and Jitkarnka, 2016), (Moralı et al., 2016), (Su et al., 2022), (Shanmugam et al., 2017), (Zhai et al., 2022), (Park et al., 2016). However, few studies have examined purun tikus (*Eleocharis dulcis*) for pyrolysis. Consequently, this research represents an inaugural exploration of the pyrolysis procedure involving purun tikus (*Eleocharis dulcis*). Purun tikus is a common plant species in the Indonesian swamplands. It exhibits robust growth characteristics, particularly under acidic conditions. So far as we know, this is the first time that the pyrolysis of purun tikus (*Eleocharis dulcis*) and its detailed reaction rates have been investigated. Studying reaction kinetics is important for understanding the mechanism of chemical reactions. Thus, this study evaluated purun tikus (*Eleocharis dulcis*) degradation, activation energy, and pre-exponential components during pyrolysis.

2. Materials and methods

2.1. Feedstock

The material for this study was originated from Danau Seran, South Kalimantan, Indonesia. (Muhakka et al., 2020) found a crude protein (8.22%), fiber (25.72%), ether extract (0.48%), ash (15.13%), hemicellulose (19.74%), cellulose (21.80%), and lignin (28.04%) in purun tikus. Material was manually cleaned, and leaves were chopped off and dried in a 105 °C oven for 24 h before usage. After grinding and sieving, a 0.25-mm sample was obtained.

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2.2. Experimental

The purified purun tikus material was heated in a specialized reaction vessel using thermal pyrolysis. The specifications of the vessel are detailed in the literature (Amrullah et al., 2022a, 2021). Stainless steel pyrolysis reactors have electric furnaces, thermocouples, PID temperature controllers, and condensers. Nitrogen gas eliminated air and oxygen before pyrolysis. Slow pyrolysis was done at 400–600°C for 10–50 min. After pyrolysis, bio-oil has been separated from solid products and yielded by dividing the product mass by the purun tikus feedstock mass.

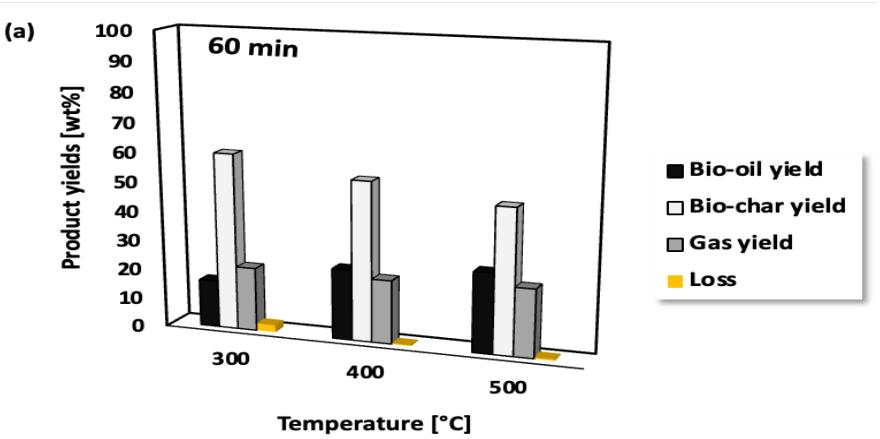
2.3. Analysis

The thermal stabilities of the purun tikus and biochar were tested using thermogravimetric analysis (TGA 4000, PerkinElmer). A few milligrams sample (8 mg) were put in an alumina crucible and prepared from room temperature to 800 °C at 10 °C/min. Nitrogen gas (50 mL/min) was used to keep the environment inert. Gas chromatography and mass spectrometry (GC/MS-QP2010 SE–Shimadzu, Japan) with a Rtx®-5MS capillary column were used to study bio-oil. Before the bio-oil was put into the GC/MS, it was mixed with dichloromethane in a ratio of 1:4 by volume (v/v). For one minute, the oven was heated to 40 °C. The temperature was then raised at a rate of 10 °C per minute for a few minutes, until it hit 150 °C. The temperature rose at a rate of 10 °C per minute until it hit 300 °C, where it stayed stable for 30 minutes. The device was kept at 250 °C as the last step. Up to 1 mL of bio-oil that had been dissolved was put into the GC/MS. The mass spectra in the NIST2008 c2.0/Xcalibur data set were used to figure out what chemicals make up bio-oil.

3. Results and discussion

3.1. Effect of Temperature and Time on Product Distribution

This study examined the effects of temperature and time on bio-oil, biochar, and gas generation. **Figure 1** depicts variations in bio-oil, bio-char, and gas yields as temperature and time change in the slow pyrolysis of purun tikus. It is important to note that bio-oil production significantly increased as the temperature increased from 300 °C to 500°C. This shift can be linked to the enhanced degradation of the purun tikus biomass.



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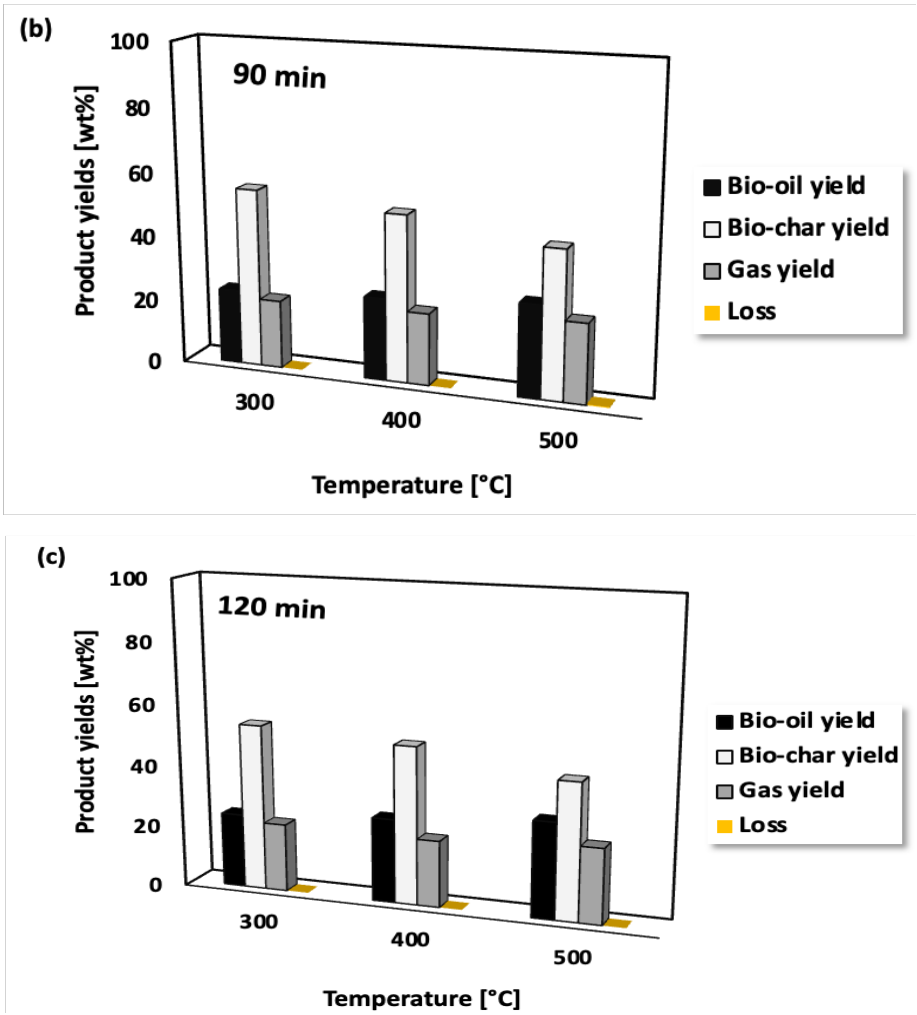

Figure 1. Effect of temperature and time on products distribution

Despite the temperature reaching 500 °C, there was no enhancement in the bio-oil production. This could be because the bio-oil was heated to temperatures exceeding 400°C, causing it to transform into a gas. This outcome is consistent with the research conducted by Park et al. (2019) and Aboulkas et al. (2017), who observed an increase in the bio-oil yield from 400 °C to 500 °C, followed by a decline at higher temperatures. Bio-oil production was significantly improved by increasing the reaction time from 60 to 120 min, from 16.05 to 24.2% at 300 °C, and from 24.2 to 27.2% at 400 °C. At 500 °C, similar to the behavior observed at 400 °C, increasing the reaction period from 60 to 120 min resulted in higher bio-oil production (from 27.2% to 31.2%). Higher temperatures and longer reaction times may be associated with cracking of the pyrolysis gases.

Previous studies by Amrullah et al. (2021) identified acetic acid, hydroxyacetone, phenol, and furfural as the primary components of purun tikus bio-oil. Simultaneously, byproducts of phenolic

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compounds were also evaluated and compared with previous studies using digestate (Tan et al., 2022) and empty fruit bunches (Idris et al., 2021) as feedstock, as shown in **Figure 2**.

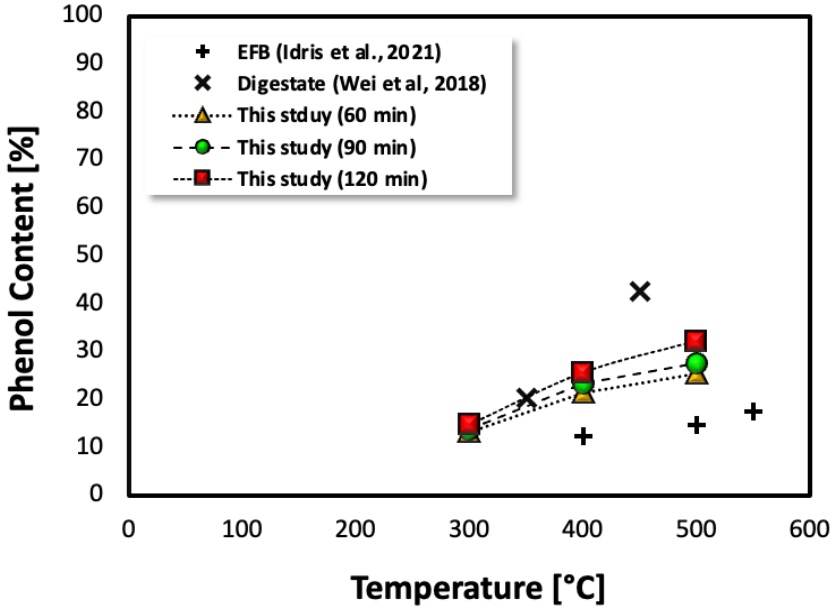

Figure 2. Comparison phenol-rich bio-oil from co-pyrolysis purun tikus (*Eleocharis dulcis)*

The observed trend indicated a positive correlation between temperature and phenol concentration, with an increase of approximately 10–30%. The obtained results display a higher percentage than that of the initial EFB raw material, which typically ranges from 10% to 18%. This phenomenon can likely be attributed to variations in raw material processing methods and essential characteristics. Digestate and this material differ in phenol content, with the latter demonstrating a more significant concentration, ranging from 18% to 40%. The probable reason for this is the high concentration of organic components within the product. According to (Amrullah et al., 2019), biomass lignin content, feedstock type, and pyrolysis process affect the concentration of phenolic compounds in bio-oil.

3.2. The calculation of reaction rate parameters

Determining reaction rate parameters is crucial for understanding biomass solidification and the process kinetics during pyrolysis. The model illustrating the process of solid destruction during the slow pyrolysis of purun tikus (*Eleocharis dulcis*) is presented in **Figure 3**.

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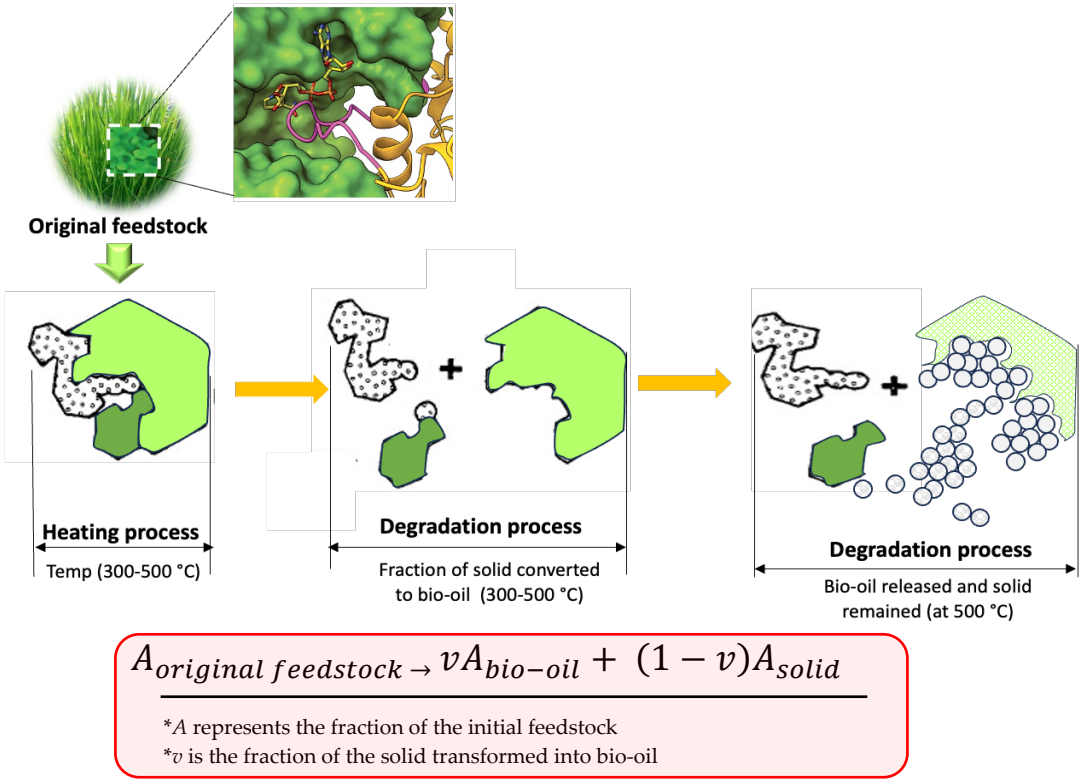

Figure 3. A conceptual model depicting the process of solid degradation of purun tikus (*Eleocharis dulcis*)

In addition, the degradation of solid processes corresponds to a first-order reaction model, and it is possible to identify the ratio and reaction rate constant associated with the decomposition of solids. A mathematical model can be formulated based on the solid degradation process illustrated in **Figure 3**. By assuming a first-order reaction, the differential equation can express reaction rate:

$$\frac{d\,[A_{purun\ tikus}]}{d_t} = -k\,[A_{purun\ tikus}] \quad (1)$$

$[A_{purun\ tikus}]$ is the concentration of $A_{purun\ tikus}$

The mass balance is assumed to be constant. The concentration of $A_{purun\ tikus}$ is expressed as

$$[A_{purun\ tikus}] = \frac{1-v}{v}[A_{bio-oil}] \quad (2)$$

Thus, based on mass balance, we obtain

$$[A_{purun\ tikus}]t - \left[1 + \frac{1-v}{v}\right][A_{bio-oil}] = [A_{purun\ tikus}]t - \frac{1}{v}[A_{bio-oil}] \quad (3)$$

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By substituting and simplifying, the equation can be expressed as

$$\frac{d}{dt}\left(\frac{[A_{bio-oil}]}{[A_{purun\ tikus}]t}\right) = vk - k\frac{[A_{bio-oil}]}{[A_{purun\ tikus}]t} \quad (4)$$

The yield of bio-oil is expressed as

$$Yield\ bio-oil = \frac{[A_{bio-oil}]}{[A_{purun\ tikus}]t} \quad (5)$$

The reaction rate constant can be stated as follows, assuming Arrhenius behavior:

$$k = k_0 exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

where k_0, Ea, R, and T are the pre-exponential factor, activation energy, gas constant, and absolute temperature, respectively. After solving the equation, the liquid yield can be expressed as

$$Yield\ of\ bio-oil = v - (v - yield\ biooil, i)\ exp\left(-k_0 exp\left(\frac{-E_a}{RT}\right)t\right) \quad (7)$$

The least-squares error (LSE) technique was applied to calculate both the reaction rate constant and the quantity of solid transformed into a liquid. **Figure 4** shows the results of fitting the experimental data to the estimated value for the correlation between the temperature and bio-oil yield. As shown, the experimental and calculated data fit well.

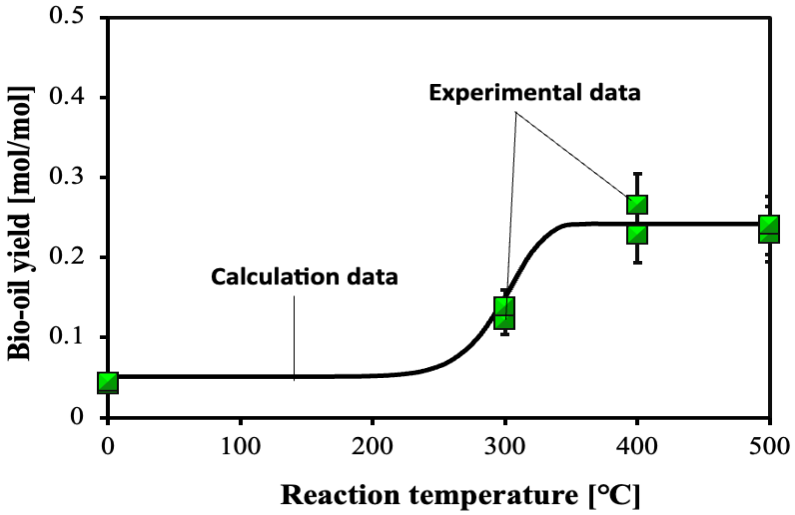

Figure 4. Curve fitting for bio-oil yield in purun tikus slow pyrolysis at different temperatures.

In addition, parity plots confirmed this, leading to a high R^2 (coefficient of determination) of 0.9982. **Figure 5** shows the Arrhenius plot of the purun tikus (*Eleocharis dulcis*) degradation rate during

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pyrolysis. An Arrhenius plot was employed to compute the activation energy and pre-exponential factor. An estimated pre-exponential factor of 0.351 s^{-1} was found for purun tikus (*Eleocharis dulcis*) pyrolysis. In addition, the activation energy for the pyrolysis of purun tikus was determined to be approximately 43. 317 kJ mol^{-1}.

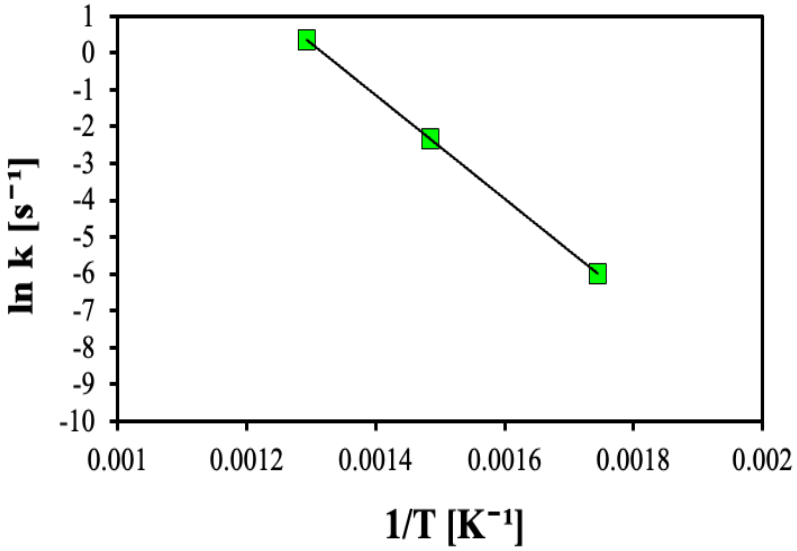

Figure 5. Arrhenius plots from experiments on purun tikus pyrolysis (300-500 ºC, 60-120 min).

This study found lower activation energy than previous experiments utilising natural biomass like coconut and almond shells. Amrullah et al. (2022c) state coconut shell pyrolysis requires 153 kJ mol^{-1} of activation energy. Furthermore, Genieva et al. (2021) also measured almond shell pyrolysis activation energy at 125.3 kJ mol-1. The chemical composition of biomass affects activation energies.

4. Conclusion

The slow pyrolysis of purun tikus (*Eleocharis dulcis*) to bio-oil was explored. Time and temperature were also studied for their potential impacts on bio-oil production. The high pyrolysis temperatures severely damage the feedstock. Pyrolysis releases purun tikus feedstock cells and boosts bio-oil production. The Arrhenius law calculates purun tikus degradation. Degradation of purun tikus has an activation energy of 43.317 kJ mol^{-1} and a pre-exponential factor of 0.351 s^{-1}.

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