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Isothermal Pyrolysis Kinetics of Various Biomass Types using Thermogravimetric Data

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Abstrak

Biomassa merupakan sumber bahan bakar terbarukan yang dapat dikonversi menjadi bio-oil sebagai sumber energi alternatif. Bahan baku biomassa yang memiliki potensi tinggi dalam pembuatan bio-oil adalah sekam padi, eceng gondok, dan tongkol jagung. Penelitian ini dilakukan untuk mengkaji pembuatan bio-oil dari berbagai biomassa menggunakan metode pirolisis dengan menggunakan variasi beberapa variabel diantaranya yaitu suhu operasi (450ºC dan 550ºC), ukuran partikel (-2 mm/+1 mm dan +2 mm), dan jenis biomassa. Berdasarkan hasil penelitian, perolehan bio-oil yang tinggi yaitu 49,06 % pada biomassa tongkol jagung dengan ukuran +2 mm pada suhu operasi 450ºC. Penyusunan model kinetika dilakukan dengan mengamati perubahan massa per satuan waktu. Pendekatan model kinetika dengan menggunakan orde 1/3 mampu menghasilkan nilai yang hampir mendekati data penelitian. Adapun hasil penyusunan model kinetika diperoleh nilai energi aktivasi proses pirolisis untuk sekam padi yaitu berkisar (24,55 – 27,79) kJ/mol, untuk tongkol jagung berkisar (35,51 – 42,55) kJ/mol, untuk eceng gondok bagian daun berkisar (23,55 – 30,72) kJ/mol, untuk eceng gondok bagian batang berkisar (30,11 – 46,77) kJ/mol, dan untuk eceng gondok campuran berkisar (35,72 – 40,70) kJ/kmol.

Kata kunci: biomassa, pirolisis, bio-oil, model kinetika, energi aktivasi

Abstract

Biomass is a renewable fuel source that can be converted into bio-oil as an alternative energy source. The type of biomass with the potential to produce bio-oil is rice husks, water hyacinths, and corn cobs. This study was conducted to examine manufacture of bio-oil from various biomass using the pyrolysis method using a variety of several variables, including operating temperature (450ºC and 550ºC), particle size (-2 mm/+1 mm and +2 mm), and type of biomass. It was observed that corn cobs yielded the highest output with 49.06% with a size of +2 mm at an operating temperature of 450ºC. The preparation of kinetic models is carried out by observing changes in mass per unit of time. The kinetic model approach using the order of 1/3 is able to produce values that are almost close to the research data. The results of kinetics model preparation obtained energy value of activation of the pyrolysis process for rice husks, which ranges from (24.55 – 27.79) kJ/mol, for corn cobs ranging from (35.51 – 42.55) kJ/mol, for water hyacinths with leaves ranging from (23.55 – 30.72) kJ/mol, for water hyacinths with stems ranging from (30.11 – 46.77) kJ/mol, and for mixed water hyacinths ranging from (35.72 – 40.70) kJ/kmol.

Keywords: biomass, pyrolysis, bio-oil, kinetic model, activation energy

1. Introduction

Population growth has driven increasing needs in the energy sector. Meanwhile, reserves of conventional energy sources derived from fossil fuel continue to depletion. In addition, emissions from the use of fuels from petroleum can damage the environment, such as the greenhouse effect and acid rain. Therefore, a renewable energy source is needed that can be guaranteed to be sustainable and safe for the environment. One of the most potential alternative energy sources is biomass waste. Where the potential of this biomass waste is predicted to be able to produce energy of 1.08 x 1011 toe (tons of oil equivalent) or 10 times the current energy needs (Sikiru, et al., 2024; Kan, Strezov, & Evans, 2016).

Several biomass waste that has the potential as an energy source includes rice husks, corn cobs, and water hyacinth. Each ton of rice will produce around 20%-weight of rice husks with a higher heating value (HHV) energy content of around 14.5-15.7 MJ/kg and a lower heating value (LHV) of around 14.2-15.5 MJ (Hendriyana, 2020). Corn cobs are waste that is rarely utilized. Currently, corn cobs are more widely developed for pellets, because corn cobs contain cellulose, hemicellulose, and lignin (Nugroho, Muhazir, & Asrori, 2024). Water hyacinth is a very fastgrowing aquatic plant. Five thousand seeds can be produced from one water hyacinth plant and can sink to the bottom and can survive for decades (Bote, Naik, & Jagadeeshgouda, 2020).

Fuel oil from rice husk biomass, corn cobs and water hyacinth can be done through thermal cracking or pyrolysis. This fuel oil called bio-oil. Bio-oil produced from the biomass pyrolysis process is usually a thick and corrosive liquid that has a dark brown color. In addition, bio-oil has a very complex chemical composition with its contents

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consisting of furan, aromatic hydrocarbons, aldehydes, ketones, phenols, esters, nitrogen compounds, anhydrosugars, organic and inorganic compounds (Abu Bakar & Titiloy, 2013).

(Fardhyanti, et al., 2019) studied the pyrolysis of 35 mesh rice husks at temperatures of 500°C and 600°C, where the bio-oil produced contained phenolic compounds of 47.98% and 62.65%-mass. The bio-oil from the pyrolysis of rice husks at a temperature range of 300°-400°C contains many methyl ester components (Novita, et al., 2022). Meanwhile, pyrolysis of 0.7-2.0 mm corn cobs at a temperature of 400°C produces bio-oil with a high acetic acid content of 37.49%-mass (Santi, Pertiwi, Matovanni, Cakradetha, & Suriyanto, 2025). For pyrolysis of water hyacinth, it has been carried out by (Ratnani, Widiyanto, & Mel, 2021) at operating conditions of 400 °C and 683°C.

The above studies have not studied the effect of size, pyrolysis temperature and pyrolysis kinetics on rice husk, corn cob and water hyacinth biomass. Therefore, this study focuses on the study of the effect of operating variables of size and temperature on bio-oil yield and discussion of pyrolysis kinetics.

2. Materials and Methods

2.1. Materials

The biomass used in this research were rice husks, corn cobs, and water hyacinth. Rice husk was obtained from rice mill in Cimahi, West Java. The corn cobs used were taken from local farmers in the area Cimahi, West Java. Meanwhile, water hyacinth obtained from Saguling, West Java.

2.2. Pre-treatment

The biomass size used in this study was -2 mm/+1mm which means the particles have an average diameter of 1.5 mm and +2 mm which means the particles have a diameter of 2 mm. Size reduction was carried out starting from grinding (Figure 1.a) followed by sieving (Figure 1.b).

(a)

(b)

Figure 1. (a) Grinding, and (b) Sieving

After the size reduction is done, the biomass is dried using natural heating from sunlight for 1-3 days. This aims to reduce the high air content in the biomass. High misture content (MC) can cause the use of energy for pyrolysis to be very large, considering the latent heat of water is very large. In addition, the bio-oil obtained has a low calorific value.

The biomass that has been dried in the sunligt, then analyzed for its moisture content by heating it using an oven until a constant biomass weight is obtained. The moisture content in biomass is calculated using the following equation (1).

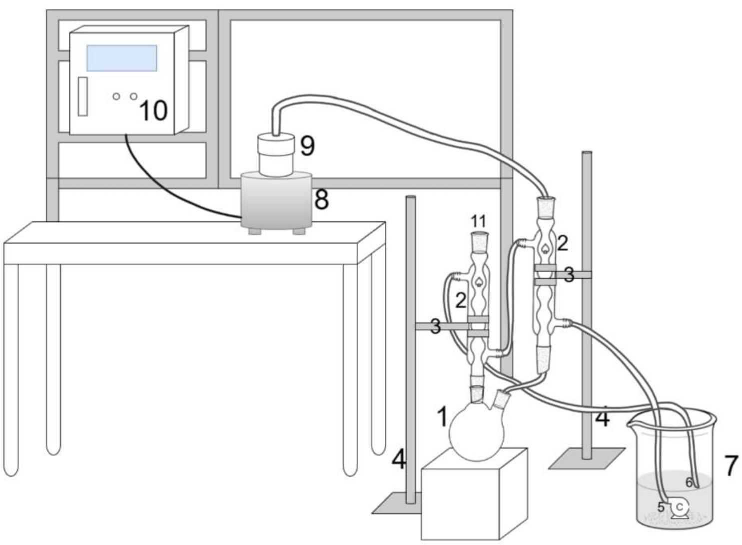
$$MC\ (\% - wt) = \frac{w_i - w_f}{w_i} x100\% \tag{1}$$

Where, MC is the water content in biomass after the drying process using sunlight, w_i is the mass of biomass before drying, w_f is the mass of biomass after drying and reaching constant weight.

2.3. Pyrolysis

Figure 2 is experimental set up for pyrolysis process. The pyrolysis process begins with weighing the biomass. Then the reactor is heated to operating temperature. After reaching operating temperature the biomass is fed into the reactor. The pyrolysis gas is condensed in a vertical condenser. The cooling medium used for the condenser is circulated water. The bio-oil produced is collected in a flask, while the uncondensed gas is discharged into the environment. The charcoal by-product remains in the pyrolysis reactor and is removed after the operation is completed. The bio-oil and charcoal produced are then weighed. Meanwhile, the weight of the gas is obtained by calculating the mass balance. The mass balance equation for calculating gas is presented in equation (2) below.

Mass of Gas = Mass of Feed – Mass of Bio oil – Mass of Charcoal (2)



Description of the Apparatus:

1. Flask
2. Condenser
3. Clamp
4. Stand
5. Water Cooling in
6. Water Cooling out
7. Cooling Systems
8. Electrical Furnace
9. Reactor
10. Controller
11. Uncondensable gas out

Figure 2. Experimental set up for isothermal pyrolysis

The yield of each product is calculated using equations (3) to (5) as follows:

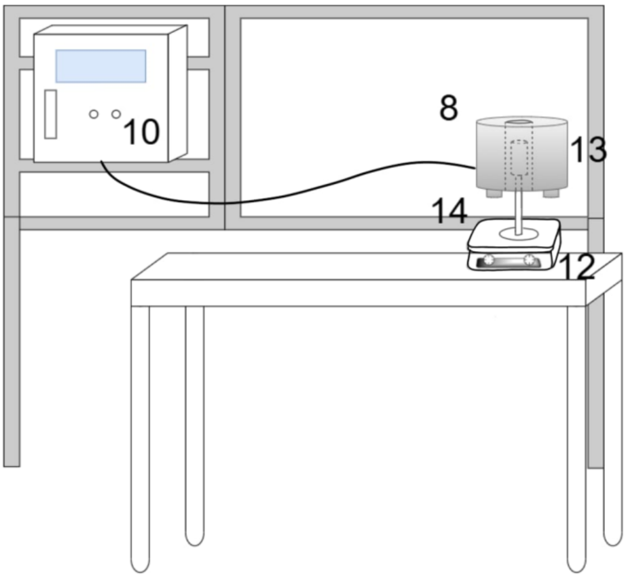
$$Y_{bio-oil}\,(\%) = \frac{mass\ of\ bio-oil}{mass\ of\ feed} x100\% \quad (3)$$

$$Y_{charcoal}\,(\%) = \frac{mass\ of\ charcoal}{mass\ of\ feed} x100\% \quad (4)$$

$$Y_{gas}\,(\%) = 1 - Y_{bio-oil}\,(\%) - Y_{charcoal}\,(\%) \quad (5)$$

2.4. Kinetics

Pyrolysis kinetics study experiment under isothermal conditions using experimental equipment with configuration as shown in Figure 3. First step, wire mesh support is placed on the analytical balance. Second step, some biomass is weighed and inserted into the wire mesh. Third step, the reactor operating temperature is set (450 and 550˚C). Fourth step, biomass is inserted into the reactor after reaching the operating temperature and mass changes are observed on the analytical balance every 5 seconds.



Description of the Apparatus:

8. Electrical Furnace
10. Controller
12. Analytical Balance
13. Wire Mesh
14. Support of wire mesh

Figure 3. Experimental set up for isothermal pyrolisis kinetics study

3. Results and Discussion

3.1. Biomass Characteristics

The characteristics of biomass have a significant influence on the pyrolysis process. Water content is one of significant characteristic that require careful evaluation due to its influence on thermal conversion efficiency. The water content in biomass will affect the speed of heat increase in the pyrolysis process, the higher the water content in the biomass, the slower the heating process because the heat source will be used more to evaporate water from raw materials (Rizal, et al., 2020). Consequently, it is important to reduce the water content of the biomass used as raw materials in the pyrolysis process. Heating using direct sunlight is used to reduce the water content in the biomass.

Based on Table 1, it can be seen that the initial water content of biomass (rice husk, corn cob and water hyacinth) is very high. Therefore, drying with sunlight is carried out for rice husk material for 1 day, corn cob for 2 days and water hyacinth for 3 days with a drying time limit indicated by a constant mass change. As a result, the water content of several biomass decreased drastically, especially after milling and sieving. This is because the surface area of biomass is smaller, contact with unsaturated air is much faster than biomass that is still in the form of lumps.

Table 1. Biomass Moisture Content for Rice Husk, Corn Cob and Water Hyacinth

Biomass	**MC (%)**			
	Initial	**Sun light**	**Drying after grinding and sieving**	
			-2 mm /+1 mm	**+2 mm**
Rice husk	9.16	4.55	4.55	4.00
Corn cob	74.08	68.54	4.00	7.69
Water Hyacinth (Leaves)	86.00	46.81	6.25	6.25
Water Hyacinth (Stem)	97.00	81.69	6.67	5.88
Water Hyacinth (Mixture)	90.00	57.41	11.11	13.33

Proximate and ultimate analysis on each type of biomass used are presented in Table 2 below. The highest content in biomass is volatile matter with a value of 57.96% in rice husks, 72.9% in corn stalks and 64.27% in water hyacinths. The hemicellulose content in raw materials is also shown in Table 3, in rice husk biomass and corn cobs, the cellulose content is the highest with 45.8% and 45%, while in water hyacinth the hemicellulose content is the highest with a value of 40.2%.

Tabel 2. Proximate Analysis and Ultimate Analysis

	Rice Husk	Corn Cob	Water Hyacinth
Proximate Analysis (% mass)			
Moisture Content	7.85	7.2	6.25
Volatile Matter	57.96	72.9	64.27
Fixed Carbon	13.52	9.6	15.93
Ash	20.67	10.3	13.27
Ultimate Analysis (% mass)			
C	35.7	43.2	39.15
H	4.48	6.92	5.475
O	31.30	49.55	40.67
N	0	0.14	1.48
S	0.05	0.19	0.15
Reference	(Harnowo & Yuonaidi, 2021)	(Singh, Patil, Tekade, Gawande, & Sawarkar, 2021)	(Tran, et al., 2021)

Tabel 3. Lignocelullose Component

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Rice Husk	45.8	16.9	17.2	(Jiang, Du, & Wang, 2021)
Corn Cob	45	35	15	(Chong, Law, & Chan, 2020)
Water Hyacinth	17.6	40.2	7.2	(Tran, et al., 2021)

3.2. Effect of Temperature and Biomass Size on Product Yields

Based on the research results by varying the operational variables, the type of biomass were rice husk, corn cob and water hyacinth, size and operating temperature, the main product obtained from the pyrolysis results is bio-oil and by-products are charcoal and combustible gas (see Figure 4). Table 4 shows the yield of the main product bio-oil and the by-products charcoal and gas at various operating variables.

Figure 4. Products of Pyrolysis: (a) Bio-Oil, (b) Charcoal, and (c) Combustible Gas.

Table 4 shows the yield of bio-oil as the expected main product varies for each type of biomass, size, and operating temperature. The bio-oil obtained in the pyrolysis process is affected by lignocellulose content in biomass. The content of hemicellulose and cellulose will form a volatile substance and will be decomposed at the beginning of the pyrolysis process while the content of lignin in biomass will produce a solid product (Rhomadoni, Jamilatun, Idris, & Setyawan, 2024).

Biomass with high lignin content tends to produce low bio-oil yield, while biomass with high cellulose content tends to produce high bio-oil yield. In this study, it was found that corn cobs produce the highest bio-oil yield compared to rice husks and water hyacinths, this is in line with the data in Table 3, that corn cobs with the highest cellulose and hemicellulose content produce higher bio-oil yields compared to rice husks and water hyacinths.

At higher operating temperatures, most of the bio-oil yields increased. This is likely due to increased decomposition of biomass structures such as lignin, cellulose, and hemicellulose. Increasing the temperature in the pyrolysis process will enhance the lignocellulose decomposition process, consequently it can produce higher yields. In accordance with what was conveyed by (Rhomadoni, Jamilatun, Idris, & Setyawan, 2024) that lignin will decompose at 350-500ºC, causing the yield produced at a variation of 500ºC to be higher when compared to the lower temperature.

Bio-oil yield tends to increase at smaller particle sizes. It is likely that particles with small surface areas will produce rapid heat transfer, resulting in high bio-oil yields. Particle size of biomass will affect the heat and mass transfer process in the pyrolysis, the larger particles will provide a larger thermal gradient, a longer residence time thus increasing the possibility of side reaction occurring (Aini , Jamilatun, & Pitoyo, 2022).

Table 4. Yield of Bio-Oil, Charcoal and Gas with Various Operating Variables

Biomass	**Products**	**Yield (%)**			
		T = 450ºC		**T = 550ºC**	
		-2mm /+1mm	**+2mm**	**-2mm /+1mm**	**+2mm**
Rice husk	Bio-oil	29.78	33.72	43.06	42.67
	Arang	46.22	44.83	43.56	39.78
	Gas	24.00	21.44	13.39	17.56
Corn cob	Bio-oil	42.17	49.06	44.56	45.89
	Arang	29.28	27.22	24.44	27.17
	Gas	28.56	23.72	31.00	26.94
Water Hyacinth (Leaves)	Bio-oil	37.72	35.83	42.06	22.39
	Arang	38.50	40.00	35.17	39.50
	Gas	23.78	24.17	22.78	38.11
Water Hyacinth (Stem)	Bio-oil	30.89	27.78	32.11	28.56
	Arang	36.78	36.89	38.56	34.44
	Gas	32.33	35.33	29.33	37.00
Water Hyacinth (Mixture)	Bio-oil	33.56	32.67	25.11	31.78
	Arang	35.44	36.33	36.89	32.22
	Gas	31.00	31.00	38.00	36.00

3.3. Kinetics

Pyrolysis kinetic data were obtained by observing the changes in mass fraction against operating time at constant temperature. The process is divided into two zones as presented in Figure 5, zone (I) is drying and zone (II) is pyrolysis. The drying zone is identified from the difference between the initial mass and the water content in the biomass. While the pyrolysis zone is characterized by the release of volatile substances (smoke) from the biomass sample followed by a drastic decrease in sample mass, the pyrolysis process is considered to be over when no more smoke is produced in the operation.

The determination of the kinetic model of the pyrolysis process uses an approach with kinetic equations stated by (Weerachanchal, Tangsathitkulchai, & Tangsathitkulchai, 2010), this equation states that the decomposition rate of the pyrolysis process depends on any order of reaction, with the equation written as follows:

$$\text{Raw material} \rightarrow \text{Char} + \text{Volatiles} \tag{6}$$

Where k is the reaction rate constant expressed by Arrhenius, A is the pre-exponential factor, Ea is the activation energy, R is the gas constant and T is the pyrolysis operating temperature and α is the change in the mass fraction of the biomass. The decomposition rate of the pyrolysis process is defined as follows:

$$\frac{d\alpha}{dt}=k(1-\alpha)^n=Ae^{-\frac{E}{RT}}(1-\alpha)^n \tag{7}$$

The change in the mass fraction of biomass is calculated using the equation:

$$\alpha=\frac{(m_o-m)}{(m_o-m_f)} \tag{8}$$

With m_o, m_f and m express the values of the initial, final mass fraction and fraction each time.
By using data matching analysis with the reaction kinetics model, it was found that this model was not able to accurately represent the experimental data. The kinetics model II used to predict the value of the kinetic parameters of this pyrolysis reaction is:

$$\frac{d\alpha}{dt}=k\times\frac{1}{(1-\alpha)^{\frac{1}{3}}} \tag{9}$$

The kinetic model fitting results are demonstrated in Figure 6. The kinetic parameters obtained were able to obtain values that were close to the experimental data by order of 1/3. The reaction kinetic parameters obtained at each biomass and process conditions are shown in the following Table 5.

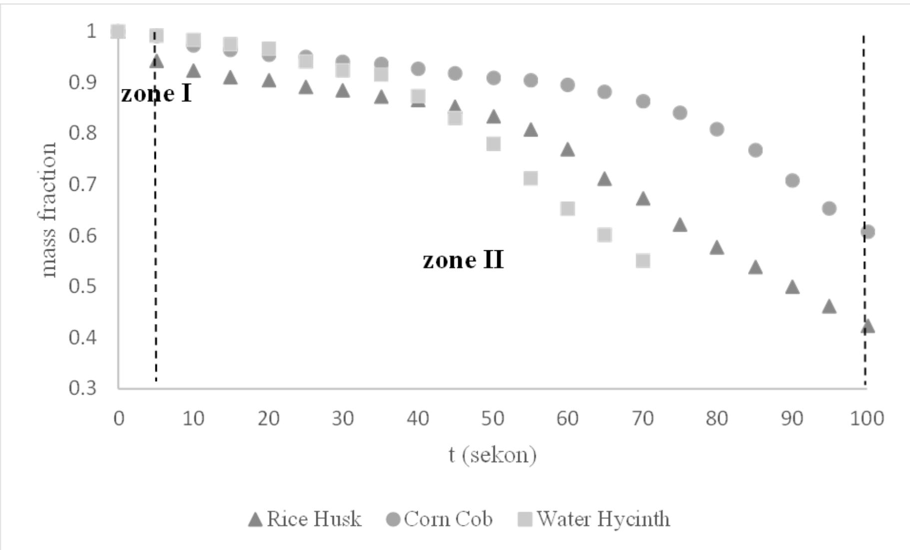


Figure 5. Mass Fraction Against Time in Operation with Size -2mm +1mm at a Temperature of 450° C

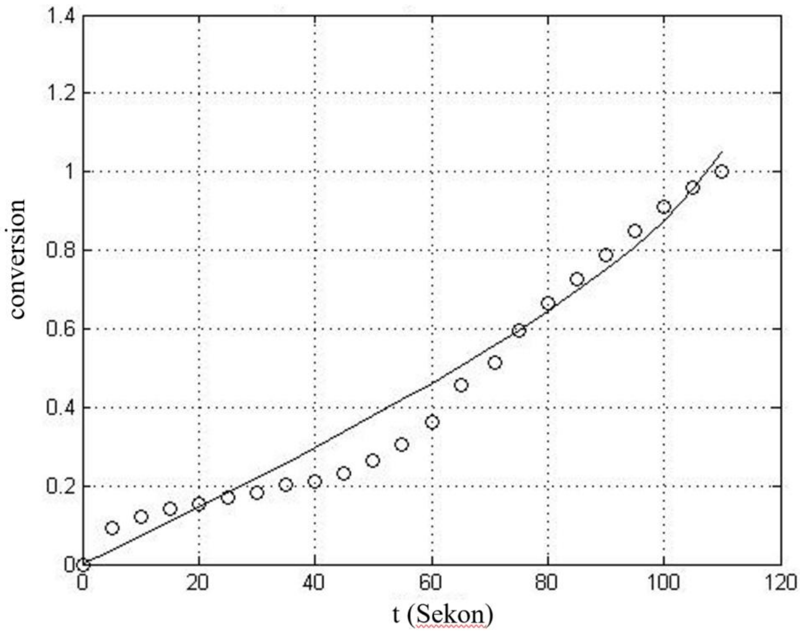


Figure 6. The Kinetics Model Fitting

Table 5. Estimated Pyrolysis Kinetic Parameters

Run	Biomass	Particle Size	Temperature (°C)	k	n	Eror	E (kJ/mol)	A
1	Rice Husk	-2mm/+1mm	450	0.007	0.3	1.103	24.55	0.42
3			550	0.0115	0.3	0.631		
2		+2mm	450	0.0065	0.3	1.879	27.79	0.66
4			550	0.0114	0.3	0.630		
5	Corn cob	-2mm/+1mm	450	0.0044	0.3	2.316	42.55	5.22
7			550	0.0104	0.3	0.949		
6		+2mm	450	0.006	0.3	2.627	35.51	2.21
8			550	0.0123	0.3	0.849		
9	Water Hyacinth (Leaves)	-2mm/+1mm	450	0.0082	0.3	0.982	23.55	0.41
11			550	0.0132	0.3	0.528		
10		+2mm	450	0.0115	0.3	0.764	30.72	1.91
12			550	0.0214	0.3	0.478		
13	Water Hyacinth (Stem)	-2mm/+1mm	450	0.0094	0.3	1.259	46.77	22.53
15			550	0.0242	0.3	0.458		
14		+2mm	450	0.0136	0.3	0.633	30.11	2.04
16			550	0.025	0.3	0.264		
17	Water Hyacinth (Mixture)	-2mm/+1mm	450	0.0102	0.3	1.443	35.72	3.88
19			550	0.021	0.3	0.481		
18		+2mm	450	0.0094	0.3	1.028	40.70	8.19
20			550	0.0214	0.3	0.162		

Based on analysis results using the kinetics model, it turns out that water hyacinths have a lower activation energy value as represented in Table 5. The energy value of water hyacinth activation obtained was 23.55 kJ/mol while rice husks were 24.55 kJ/mol and corn cobs were 42.55 kJ/mol. The mechanism of the pyrolysis reaction determines the activation energy, the low value of the activation energy will indicate that the pyrolysis reaction that occurs is proceeding faster (Rambhatla, Panicker, Mishra, Manjeshwar, & Sharma, 2025). This results supports the graphical representation in Figure 5. In the graph, it can be seen that water hyacinth decomposes faster and reaches the end of the pyrolysis process compared to rice husks and corn cobs.

Conclusions

This study indicated that the pyrolysis process was significantly influenced by the specific type of biomass utilized. The lignocellulose content present in the raw materials also contributed to an increased yield of bio-oils. Furthermore, the pyrolysis outcomes were proven to be affected by the operating parameters, particularly temperature and particle size. An increase in the pyrolysis temperature up to 500°C resulted in a higher bio-oil gain, as the decomposition of lignocellulose structures occurred more intensively. Smaller particle sizes accelerated heat transfer and shortened the reaction time, thereby increasing the yield of bio-oils.

Kinetic studies demonstrated that a 1/3rd order reaction model was best suited to describe the decomposition rate of the biomass during the pyrolysis process. Based on the preparation of this kinetic model, the activation energy values for the pyrolysis process were obtained as follows: for rice husks, the energy ranged from (24.55-27.79) kJ/mol; for corn cobs, it ranged from (35.51-42.55) kJ/mol; for water hyacinths with leaves, it ranged from (23.55-30.72) kJ/mol; for water hyacinths with stems, it ranged from (30.11-46.77) kJ/mol; and for mixed water hyacinths, it ranged from (35.72-40.70) kJ/kmol. Among the three types of biomass analyzed, water hyacinth possessed the lowest activation energy, which stood at 23.55 kJ/mol. This condition indicated that the pyrolysis process took place faster than it did for rice husks and corn cobs. Consequently, the selection of the biomass type, the initial pre-treatment, and the establishment of the appropriate operating conditions were crucial in determining the effectiveness and efficiency of the pyrolysis process for optimal bio-oil production.

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