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Palm Oil Shell Pyrolysis: Temperature Effect, Kinetics, and Thermodynamics Study

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Abstract— **Palm oil shell (POS) is a solid waste from the oil palm industry and can cause environmental problems. This waste could convert into high-quality products such as biochar, bio-oil, and biogas that follow reaction mechanisms and kinetics parameters. This study aims to characterize palm oil shells and biochar, determine the optimum temperature of oil palm shell pyrolysis to produce biochar as briquettes and obtain kinetics and thermodynamic parameters. Palm oil shells were cleaned, sifted to a size of 0.4-2 mm, and dried at 105 ºC for 24 h. The pyrolysis was operated by 200 g of POS in a pyrolysis reactor and kept at 350 ºC, 375 ºC, and 400 ºC for 1 h. The bio-oil mass was recorded every 5 min, starting from the first drop after the temperature of pyrolysis reached. The optimum temperature for charcoal briquettes was 375 ºC. The liquid and solid products were increased by increasing temperature, and gas products were decreased. The kinetics parameters of activation energy (E) and pre-exponential factor (A) were 20.7808 kJ mol^{-1} and 0.0821 min^{-1}, respectively. Palm oil shell pyrolysis requires a lot of heat which is indicated by a positive enthalpy change (ΔH) of 15.3934 kJ $mole^{-1}$. The non-spontaneous reaction on pyrolysis was proved by a positive Gibbs free energy change (ΔG) of 179.2998 kJ $mole^{-1}$. Those parameters allow the process to be operated in optimal conditions, increasing the efficiency in future studies.**

Keywords— **Pyrolysis; palm oil shells; biochar; kinetics; thermodynamics.**

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I. INTRODUCTION

South Kalimantan produces much solid waste from palm oil shells as a palm oil producer. The environmental problem of waste and depletion of fossil fuels encourage researchers to develop alternative biomass-based fuels. In refining palm oil, each ton of palm oil fruit bunches will produce about 0.7 tons of palm oil shells as solid waste [1]. Pyrolysis is a thermochemical process of degradation of organic matter to convert waste materials into energy and more valuable products [2], [3]. Biomass is one of the raw materials for pyrolysis to generate liquid (bio-oil), gas (biogas), and solid product (biochar). Lignocellulosic on biomass containing cellulose, hemicellulose, and lignin [4]. Hemicellulose degrades at 220–315 ºC that has a branched structure. Cellulose consists of linear chain polysaccharides that decompose at a temperature of 315-400 ºC. Lignin is a more complicated polymer structure that decomposes in a temperature range of 150–900 ºC [5]. Cellulose will increase bio-oil yield, lignin is the main contributor to charcoal production, and hemicellulose contributes to bio-oil and syngas yield [6]. The biomass briquettes are biomass densification in which particles are decomposed with specific variable pressure, temperature, and other processes. The products of densification have a uniform shape and size, so they can be relatively easier and cheaper to transport and store [7]. Briquettes can replace solid fuels such as charcoal, firewood, and coal.

Several researchers have been carried out for the utilization of palm oil shells such as power generation [8], activated carbon [9], supercapacitors [10], heavy metal removal [11], aggregates in concrete [12], biochar production [13], phenol synthesis [14] and various other applications. Solid charcoal (biochar) can serve as solid fuel and adsorbent [15]. Biochar's physical and chemical properties mainly depend on reaction conditions, biomass type, reactor configuration, etc. [16]. So, using palm oil shells has a potential product to develop and investigate, especially in the process. Among the parameters of reaction conditions, such as heating rate, temperature, and residence time, the most influential parameter is pyrolysis temperature, which controls biochar yield and greatly influences its characteristic [17]. In order to improve the pyrolysis product, the kinetics study is very important, related to reaction rate, reactor size, and reaction time. Therefore, it can be applied to high-volume production [18]. Moreover, the kinetic parameters allow the process to run under optimal conditions to increase efficiency. Pyrolysis kinetics study of some biomass in batch reactors have been informed, e.g. pyrolysis kinetics of castor and corn stalk [19], [20]. Soria-Verdugo et al (2018) expanded a general kinetics model of microalgae pyrolysis [21]. Thu et al (2020) simulated the formation of bio-oil through empty bunch pyrolysis using the modified kinetics equation [22].

There have not been many studies on the kinetics of palm oil shell pyrolysis. Therefore, this research will characterize and study the kinetics based on biomass conversion in palm oil shell pyrolysis using a decomposition reaction mechanism. Kinetics study was performed to obtain activation energy (E) and pre-exponential factor (A), and thermodynamic studies was carried out to determine enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS**).**

II. MATERIALS AND METHOD

A. Materials

Palm oil shell (POS) were obtained from PT. Perkebunan Nusantara XIII Pelaihari, Tanah Laut District, South Kalimantan, Indonesia, which consists of hemicellulose (18,84 %), cellulose (32,79 %) and lignin (33,745 %).

B. Pyrolysis of Palm Oil Shell

The shells were cleaned, cut into pieces, sifted to a size of 0.4-2 mm, and dried at 105 ºC for 24 h in an oven. The first step involved the analysis of lignocellulose content and the raw material's proximate and calorific value. The pyrolysis process was performed in a batch reactor (Figure 1).

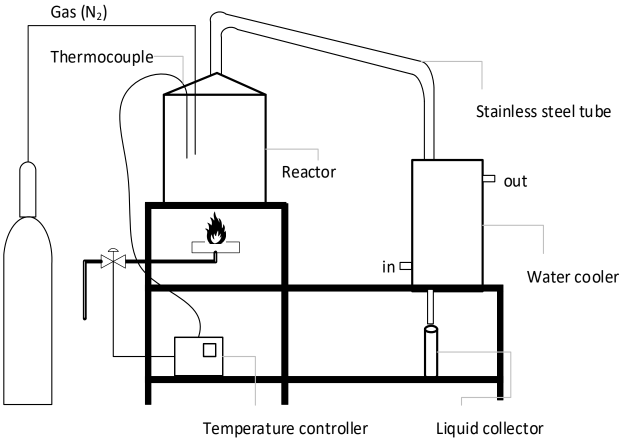


Fig. 1 Experimental apparatus for pyrolysis palm oil shell

The pyrolysis started by adding 200 g of POS in a pyrolysis reactor equipped with a pipe connected to a condenser and a container for collecting liquid products. The pyrolysis process was operated at 350 ºC, 375 ºC, and 400 ºC for 1 h with 150 mL min^{-1} nitrogen flow. Liquid mass was recorded every 5 min, starting from the first drop to 1 h after the pyrolysis temperature was reached. After the complete reaction, the reactor was cooled at room temperature, and biochar was collected. The proximate and calorific numbers from products were analyzed.

C. Kinetics and Thermodynamics Study

The kinetics study uses a single chemical reaction which assumes that the liquid, solid, and gas products occur simultaneously from the cracking of the oil palm shell (Eq. 1). The decomposition rate of palm oil shells and the formation rate of liquid and solid and gas are obtained from the mass balance of each component.

$$\text{POS} \xrightarrow{k} \text{a Liquid} + \text{b Solid} + \text{c Gas} \qquad (1)$$

Rate of decomposition of palm oil shell (p):

$$\frac{dm_p}{dt} = -k.m_p \qquad (2)$$

Rate of formation of liquid (l):

$$\frac{dm_l}{dt} = a.k.m_p \qquad (3)$$

Rate of formation of solid/biochar (s):

$$\frac{dm_s}{dt} = b.k.m_p \qquad (4)$$

Rate of formation of gas (g):

$$\frac{dm_g}{dt} = c.k.m_p \qquad (5)$$

Yield coefficient:

$$a + b + c = 1 \qquad (6)$$

Change in enthalpy (ΔH,), change in Gibbs free energy (ΔG) and change in entropy (ΔS) as thermodynamic parameters were obtained from Equations (7) - (9).

$$\Delta H = E - RT \qquad (7)$$

$$\Delta G = E + RT_m \ln\left(\frac{K_B T_m}{hA}\right) \qquad (8)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \qquad (9)$$

D. Characterization

The surface morphology was observed through a Field-emission scanning electron microscopy (FE-SEM, JOEL JSM-6500F), and the calorific number was quantified using a bomb calorimeter (Gallenkamp Adiabatic Bomb Calorimeter CBA-305). Meanwhile, the proximate analysis was determined according to ASTM D3172-07a. Thermal gravimetric Analysis (TGA) and Derivative Thermal Gravimetric (DTG) performance using a Perkin Elmer, Diamond TG/DTA was performed at 30 ºC-1000 °C under nitrogen flow with a heating rate of 10°C min^{-1}. The mass degradation function of temperature studied the content of degraded substances on the sample.

III. RESULTS AND DISCUSSION

A. Characterization of Palm Oil Shell and Biochar

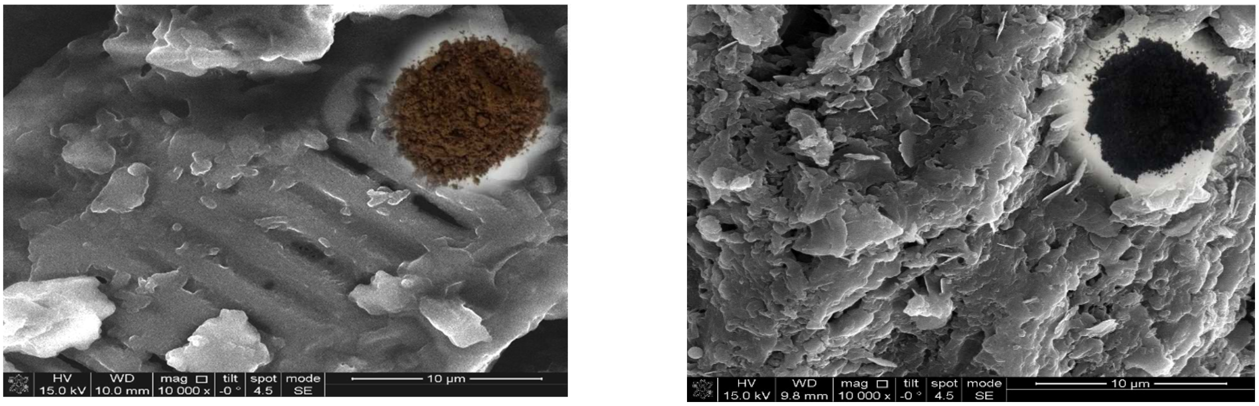
The proximate analysis and calorific value of POS and biochar are shown in Table 1. The Ash content of the POS was 3.252%, lower than castor [19] or rice husk [23]. The high ash content can affect the burning of material, which causes aggregation and fouling problems. Besides, it also affects process costs, reduced energy conversion, poor combustion, and disposal problems [24]. POS has lower moisture, less than 10% in dry conditions, and volatile content of 64%, higher than rice husk [23], which is good for combustion and gasification processes. In addition, palm oil shell contains 25.163% of fixed carbon, almost the same as rice husk [23]. The calorific value of POS was increased up to 2000 cal g^{-1} after pyrolysis. Biochar as a product by pyrolysis at 375° C could be used as briquettes because it was met all the quality requirements of charcoal briquettes, the maximum ash content and moisture is 8%, the volatile matter is 15% maximum, fixed carbon is more than 30% and the heating value more than 5000 cal g^{-1}. POS has a rash surface due to the complex structure of lignocellulose (Figure 2a). On the other hand, biochar shows a different structure, a surface-like sheet or layer in small parts, which aggregate each other. The changing structure was conducted during heating (Figure 2b).

TABLE I

PROXIMATE ANALYSIS AND CALORIFIC VALUE OF PALM OIL SHELL AND BIOCHAR

Materials	**Ash (%)**	**Moisture (%)**	**Volatile matter (%)**	**Fix carbon (%)**	**Calorific value (cal g^{-1})**
Palm Oil Shell	3.252	7.520	64.067	25.163	4738.180
Biochar 350 °C	10.533	4.465	10.681	74.323	6465.438
Biochar 375 °C	7.0345	4.478	11.213	77.276	6513.901
Biochar 400 °C	10.484	1.906	11.227	76.384	6614.277
SNI 01-6235-2000	Max 8	Max 8	Max 15	> 30	5000-6000

The original brown color of POS turns to black color after pyrolysis. It indicates the changing structure of material becomes carbon (Figure 2, inet). The surface morphology images of POS and biochar are presented in Figure 2.



(a) (b)

Fig. 2 FE-SEM Micrograph of Palm Oil Shell (a) before pyrolysis (b) after pyrolysis at 400 °C

The carbonization of POS was followed by evaporation, dehydration, carbon structure formation, and cavities or pores. The difference in morphology is also because of the different structures of the material after pyrolysis turn to carbon. Pyrolysis of shells at high temperatures tends to increase the number and diameter of pores [25]. In order to study the thermal degradation of POS, TGA and DTG analyses were carried out, which temperatures up to 1000 ºC. Fig. 3 shows 3th stages decomposition of POS, at preheating occurs at a temperature range of 40-150.6 °C for 1st stage.

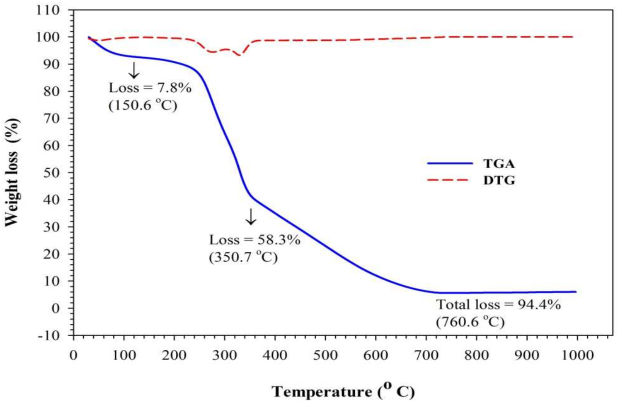


Fig. 3 TG and DTG curves of Palm Oil Shell

The removal of moisture or lighter components were a mass loss of 7.8%, then continuous slowly up to about 280 ºC. For 2nd stage indicated a mass reduction of 58.3%, due to the removal of cellulose, hemicellulose, and lignin at 350.7°C. The 3th stage final level of decomposition, is shown as a line that begins to tend to be flat and ends at a temperature of 750.6°C with a mass loss sample of 94.4%. This typical degradation is similar to other lignocellulose materials [26].

B. *Pyrolysis Products*

The mass of POS in the reactor was decreased because the shell components were broken down into liquid, gas, and solid. Figure 4 shows the typical pyrolysis product; by increasing temperature, the mass of liquid and solid products also increased, while the gas product decreased due to increased decomposition reaction rate. The increasing pyrolysis temperature from 300 ºC to 400 ºC affected the product's mass. The mass of biochar and liquid were increased about 65.92% and 26.52%, respectively. On the other hand, the production of gas decreased about 30.95%.

Based on the result, the highest temperature will yield more biochar. In addition, biochar quality is also considered for briquettes; the temperature of 375 ºC is the best condition for which a specific parameter has been fulfilled (Table 1). At higher temperatures, the heat from the particles will be greater, resulting increase in energy. So, the effect of the pyrolysis process on the decomposition of components will be more perfect because the temperature increases [27].

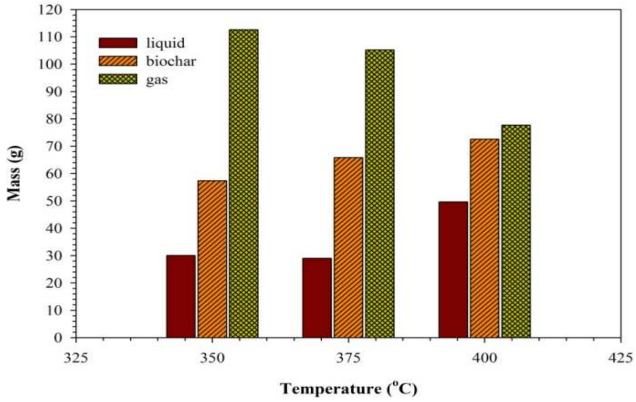


Fig. 4 Mass of Pyrolysis Products (liquid, biochart, gas) at various temperatures

C. Palm Oil Shell Pyrolysis Kinetics Study

The kinetic model used to determine the temperature effect on the kinetics of pyrolysis reaction is a single reaction. The pyrolysis products will be decomposed into three products, liquid, solid, and gas, with the same reaction rate. The liquid product was collected periodically during the pyrolysis. The yield coefficient implicitly covers product formation competition. It shows the amount of liquid, solid, and gas formed based on the basic calculation of 1 gram of POS. The advantage of this model is that it could be used for fast calculation and limitations of measured data in this study. Figure 5 shows the relationship between the mass of liquid obtained from data at various times and the mass of liquid simulated for various temperatures.

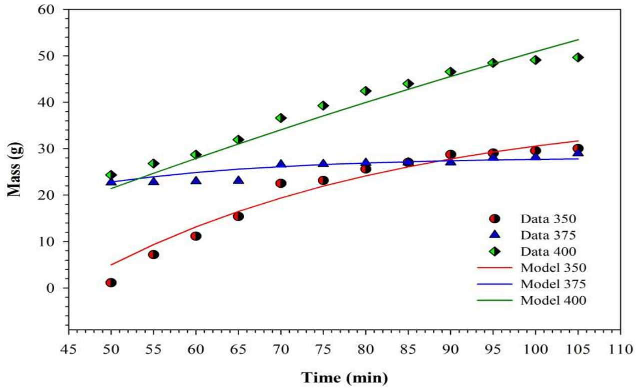


Fig. 5 The Relationship between Liquid Mass Data and Time from Experiments and Simulations

Figure 5 shows that the simulation results nearly fit with experimental data. The model's suitability is also determined by calculating the relative average error of comparing the experimental liquid mass data with simulated liquid, which is 14.67%. Based on the kinetics model, the value of the reaction rate constant (k) can be obtained, which is assumed to be the same for each of the pyrolysis products, liquids, solids, and gases at each temperature (Table 2). Furthermore, the effect of temperature on the reaction rate constant is shown in Figure 6. The higher the pyrolysis temperature, the greater the reaction rate constant (k) value, with a number reaction rate constant of 0.048 min^{-1} at 400 ºC. The values of the reaction rate constant were obtained from a mathematical model. The overall reaction rate constant is a function of the various parameters directly proportional to temperature, so the k value increases with increasing temperature [28].

TABLE II
THERMODYNAMIC DATA OF PALM OIL SHELL PYROLYSIS

T (ºC)	**k (min-^{1})**	**ΔH (kJ mole^{-1})**	**ΔS (kJ mole^{-1} K^{-1})**	**ΔG (kJmole^{-1})**
350	0.046	15.6012	-251.5947	172.3447
375	0.048	15.3934	-252.9419	179.2998
400	0.048	15.1855	-254.3609	186.3704

It is assumed that the reaction rate constant for temperature variations follows the Arhenius equation:

$$k = A.e^{-\frac{E}{RT}} \tag{10}$$

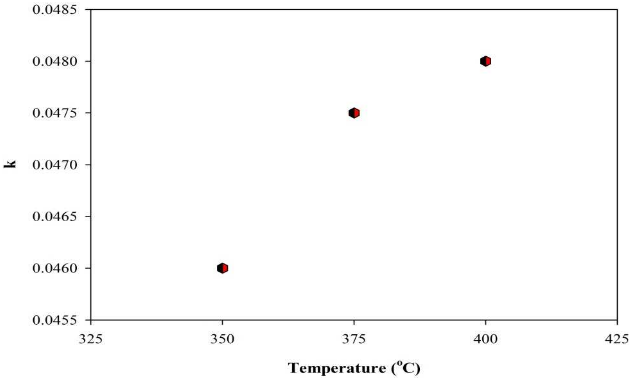


Fig. 6 Relation of a constant rate of reaction to temperature

The involved kinetic parameters (referring to pre-exponential factor and activation energy) were obtained by fitting data between ln k and 1/T, as shown in Figure 7.

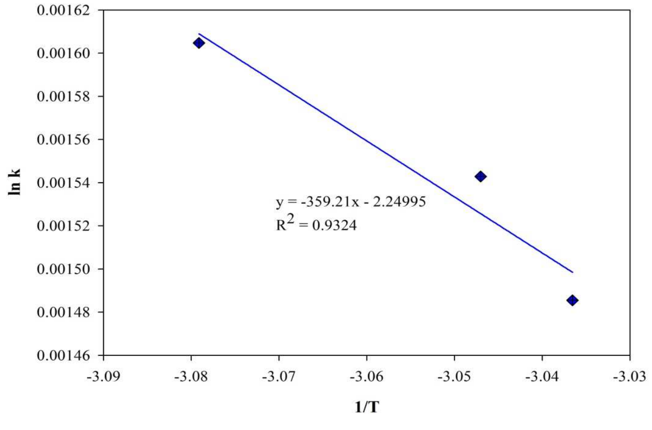


Fig. 7 Relation of ln k and 1/T

Fig 7 shows the reaction follows the Arrhenius equation. The pre-exponential factor (A) value is 0.0821 $\text{min}^{-1,}$ and the activation energy value (E) is 20.7808 kJ mole^{-1}. The activation energy of rice husk pyrolysis is about 57-83 kJ mol^{-1} and the pre-exponential factor is 230-411 min^{-1} [23], while the activation energy and pre-exponential factor of demineralized rice husk pyrolysis is about 13-16 kJ/mol and 0.456-0.972 min^{-1}, respectively [29]. The activation energy of castor pyrolysis was 192.809 kJ $\text{mol}^{-1,}$ where it contains more cellulose [19]. The activation energy for degradation of cellulose, hemicellulose, and lignin are 168.61-223.32, 73.85-

126.31, and 23.41-87.21 kJ mol^{-1}, respectively [30], [31]. Cellulose has the highest activation energy value, and lignin has the lowest [32]. It was observed that POS has more lignin content (Table 1). Therefore, less activation energy is required for decomposition. The lower E value reflects that it can be co-fired with other with higher or lower E value biomass and is suitable for converting biomass heat into value-added bioenergy [19].

The activation energy (E) is the minimum energy required to initiate the reaction. So, initiating a high activation energy reaction will be difficult [33]. Generally, the low pre-exponential factors show surface reactions. If the reaction does not depend on the surface area, a low value of the pre-exponential factor indicates a closed complex, and a simple complex was indicated by a higher value of A [34].

D. Palm Oil Shell Pyrolysis Thermodynamics Study

Thermodynamic properties can be used to determine pyrolysis reactions. It involves the change in enthalpy (ΔH), the change in entropy (ΔS), and the change in Gibbs free energy (ΔG) as a function of temperature are shown in Table 2. Enthalpy is one of the thermodynamic characteristics showing the total heat of the system. Enthalpy in the pyrolysis process represents the total energy consumed to convert biomass into various products such as oil, gas, and char [35]. The positive enthalpy change with the average value of 15.3934 kJ mole-1, so the pyrolysis reaction of palm oil shells is endothermic. It means heat is required from the environment. Gibbs free energy refers to the total energy added by the system to form an activated complex [5]. The positive value of Gibbs free energy, about 179.2998 kJ mole^{-1} indicates the pyrolysis reaction did not occur spontaneously. For general reaction, the spontaneous reaction can occur if $\Delta G < 0$.

Negative entropy values (ΔS) indicate that the products produced by bond dissociation have a lower degree of disorder than the initial reactant. The low number of entropies means the material has just undergone some chemical and physical changes and it is close to its thermodynamic equilibrium state. At this time, the material exhibits low reactivity and requires more time to form an activated complex. Otherwise, high entropy means it takes less time to form an activated complex because it shows high reactivity [19]. The entropy also describes the degree of carbon deposit arrangement in palm oil shells. All negative numbers of ΔS indicate that the activated complex of POS has a more ordered structure than the initial component. The pyrolysis process involves a disordered structure to an ordered structure [36]. In other words, a negative value of entropy change indicates a change in the particles' inaccuracy, ranging from less regular to more regular. From the thermodynamic data, it can be known that the pyrolysis process of POS requires a lot of heat (high temperature), so a decomposition reaction can occur, which is manifested as a positive enthalpy change (endothermic) and a positive Gibbs free energy change (non-spontaneous reactions).

IV. CONCLUSION

The pyrolysis process was effected to increase palm oil shell calorific value, and the change its physical properties. The POS surface morphology changed the formation of pores on biochar. By increasing temperature followed by increased liquid and solid products, and decreasing of gas product. The kinetics parameters of the pyrolysis obtained from the single reaction model are the pre-exponential factor (A) value of 0.0821 min^{-1} and the activation energy value (E) of 20.7808 kJ mol^{-1}. Palm oil shell pyrolysis requires a lot of heat, indicating a positive number of enthalpy change (ΔH) of 15.3934 kJ mole^{-1}. The number of Gibbs free energy change (ΔG) shown a non-spontaneous reaction with have number of 179.2998 kJ mole^{-1}.

NOMENCLATURE

E	activation energy	kJ mole^{-1}
A	pre-exponential factor	minute^{-1}
K_B	Boltzmann constant (1,381x10^{-23})	J K^{-1}
Tm	maximum temperature	K
H	Planks constant (6,626 x10^{-34})	J
R	ideal gas constant (8.314)	J mole^{-1}K^{-1}

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