



Original Research Article

Investigating Kinetic and Thermodynamic Parameters in the Pyrolysis of Sheep Manure Using Thermogravimetric Analysis

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ABSTRACT

The kinetics of the pyrolysis process of sheep manure were investigated using Thermogravimetric Analysis in this work. It was heated at 30°C to 900°C with a heating rate of 10°C/min. There are two stages of mass degradation, namely dehydration and devolatilization. The temperature dehydration stage is 30°C–140°C while the devolatilization stage is 210°C–900°C. However, at temperatures >500°C, mass degradation decreases until it reaches 900°C. This indicates that most of the volatile matter has disappeared at this temperature. The devolatilization stage includes the decomposition of hemicellulose and cellulose (210°C–900°C) and lignin (>590°C). The calculated activation energy from Friedman's non-conversional method is 21.32 kJ/mol and Coats-Redfern is 26,20 kJ/mol, while the frequency factor value is $9.94 \cdot 10^{18} \text{ s}^{-1}$ for Friedman and $3.42 \cdot 10^{18}$ for Coats-Redfern Method which indicates that the pyrolysis process of sheep manure is a complicated phenomenon. The estimated activation energy value is then used to calculate thermodynamic properties e.g., Gibbs free energy, enthalpy, and entropy.

KEYWORDS

Pyrolysis, Sheep manure, Thermogravimetric, Kinetic, Friedman.

INTRODUCTION

Global warming refers to the occurrence of increasing average temperatures on Earth caused by the emission of greenhouse gases into the atmosphere. Currently, global warming is an important issue that concerns the world. It significantly impacts climate and the environment, including rising global average temperatures, alteration in extreme weather, and sea level. This raises global concerns over its impact on human life and ecosystems. According to Indonesian Meteorological, Climatological, and Geophysical Agency, one such impact can be observed in Indonesia, where there is an average temperature anomaly in April 2023, showing a positive anomaly with a value of 0.2°C.

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On a global scale, according to the National Oceanic and Atmospheric Administration (NOAA) website, April 2023 is the fourth warmest month in the world in NOAA's 174-year history.

Therefore, it is necessary to address climate change and support one of the Sustainable Development (SDGs) program's goals, tackling climate change.

One of the contributors to carbon emissions is animal waste, one of them is manure. Animal manure contributes approximately 10% of carbon emissions to the total emissions, which includes CO₂, CH₄, and N₂O [1]. Up to 2020, only 11% of biomass was used as a renewable energy source [2]. Similarly, just 1.64% of animal waste and 4.3% of biomass are used as renewable energy sources in Indonesia [3]. One of the benefits of using biomass as a sustainable energy source is that it grows quickly and is abundant. The quantity of manure produced by livestock such as sheep, goats, and cattle can vary depending on factors such as feed type, age, body weight, and animal health. Animal waste generally exists in solid, liquid, and gas forms.

Solid manure, including sheep and goat manure, typically have a lower moisture content of around 70-80%. Meanwhile, cow manure usually has a higher moisture content of around 85-90%. The composition of solid manure primarily consists of organic materials such as fiber, protein, and carbohydrates that are not digested by the livestock's digestive system. Sheep and goat solid manure contain more nitrogen and phosphorus compared to cow manure. The amount of manure produced by sheep weighing 20-40 kg is approximately 0.32 to 0.625 kg per day, equivalent to 0.3 tons per year [4]. The potentials for renewable energy sources from biomass will increase in line with the growth of the livestock population [5]. Sheep manure contains a higher volatile content (58–64%) compared to cow manure (53%). Consequently, when it is converted through pyrolysis, sheep manure can produce higher biochar and syngas yield than cow manure. Furthermore, when compared to other manures, sheep manure have a higher fixed carbon composition (approximately 13%), implying a greater calorific value [6].

Methods used to convert biomass energy are gasification, pyrolysis, and combustion. The fuel can be totally oxidized and transformed into heat during the combustion phase. However, the efficiency of this combustion process is merely 10%, leading to environmental pollution as a consequence [4]. On the other hand, gasification involves a partial oxidation process of biomass and conversion of the biomass into fuel in gas. Pyrolysis is a thermal decomposition process using heat energy with little or no oxygen [7]. The main advantage of the pyrolysis is its adjustability according to the desired results.

To acquire a thorough comprehension of biomass pyrolysis, it is essential to also comprehend the thermal performance of the feedstock and its components [8]. The conversion of biomass into high-value products relies heavily on the rate of pyrolysis kinetics [9]. Further study of biomass properties requires analysis of Arrhenius parameters. The Arrhenius parameters of the thermal degradation process are essential for design optimization, understanding reaction mechanisms, and predicting thermodynamic features for effective biomass energy production [8]. Determining the Arrhenius parameters involves conducting measurements and thermal analysis of biomass in a controlled environment, which can be achieved through thermogravimetric analysis (TGA) technique. The TGA test results provide information about the extent of thermal degradation of biomass at various temperatures. By obtaining Arrhenius parameters, such as reaction rate constant, activation energy, and frequency factor, it is also possible to understand the kinetics of biomass pyrolysis. This is crucial for designing efficient pyrolysis processes, understanding the involved reaction mechanism, and predicting the relevant thermodynamic properties for efficient energy generation from biomass.

Micro-scale investigation of biomass can be accurately conducted through Thermogravimetric Analysis (TGA) to determine its thermal characteristics. The results of this analysis can be utilized to establish operational parameters that enhance pyrolysis efficiency [10]. Moreover, TGA is widely employed for studying pyrolysis kinetics, particularly in conditions with low heating rates, as it offers high precision [11]. Pyrolysis kinetics modeling can be achieved through three model approaches: two-stage semi-global, one-stage multiple reactions, one-stage global single reaction [12]. These models rely on the Arrhenius theory, necessitating information about kinetic parameters e.g. frequency factor, reaction model,

activation energy [10]. Therefore, investigating the kinetic parameters of pyrolysis requires Thermogravimetry Analysis.

Previously, several studies had been carried out on reaction kinetic analysis for several animal wastes. Chong et al. studies on reaction kinetic analysis of horse manure revealed promising parameters for modeling devolatilization and designing thermochemical conversion processes, indicating its potential for bioenergy recovery including horse [13]. Xinsong Yuan et al. investigated the multi-stage nature of the cattle manure pyrolysis process, characterized by interactions between various components, elucidated through thermogravimetric analysis and isoconversional methods, providing valuable insights for reactor design and understanding the pyrolysis mechanism [14].

The study conducted by Xiaodong Pu et al. elucidated the thermal decomposition characteristics and kinetics of chicken manure, revealing significant differences between nitrogen and air atmospheres. The optimal thermal decomposition was achieved under a 10°C/min heating rate, with distinctive activation energies observed under different atmospheric conditions [15]. Conversely, Zeynep Yıldız et al. utilized operating conditions with a heating rate ranging from 5 to 20 °C/min [10]. Prakash Parthasarathy et al. concluded that the study on the sustainable valorization of camel manure through thermogravimetric analysis provided valuable insights into the kinetics and thermodynamic properties of O₂ gasification, which can inform the design and optimization of gasifiers for efficient utilization of this waste resource [16]. Conversely, their studies on the pyrolytic behavior of camel manure elucidated the effects of heating rates on thermal characteristics and char yield, although it showed an insignificant impact on the kinetic parameters, providing valuable insights for the design of pyrolysis reactors [17]. Apart from that, Muhammad et al. explored and compared the pyrolytic conversion of the dairy manure of two common milch animals (cow and buffalo) within confined animal feeding operations through detailed kinetic and thermodynamic analysis [18]. Hui Wang et al. concluded that optimal performance of pyrolysis made from swine manure can be achieved at a pyrolysis temperature of 550°C and a reaction time of 1 second [19]. Furthermore, Fernandez et al. studied swine manure and revealed consistent kinetics of pyrolysis and combustion processes, with the distributed activation energy model proving to be the most accurate for predicting weight loss curves [20]. However, to our knowledge, there has been no study on the reaction kinetics of pure sheep manure (without mixture). Research conducted by Zuhair Akyürek (2021) analyzed the reaction kinetics in the co-pyrolysis of sheep manure with recycled polyethylene terephthalate [13]. Focusing on sheep manure allows kinetic research to understand the reaction mechanism more profoundly. This includes determining the activation energy, reaction rate, and phase changes that occur during the pyrolysis process. A better understanding of the kinetics of these reactions is essential for optimizing pyrolysis process parameters and increasing the efficiency of converting feedstocks into desired products.

Many TGA studies have been carried out on animal waste. Erdogdu et al. (2018) observed through their TGA analysis that the maximum separation rate occurred in the temperature range of 250 to 500°C, with complete conversion being achieved at approximately 600°C [4]. Parthasarathya et al. (2022) conducted a study that explored the bio-energy potential of kinetic models. This investigation involved the assessment of their physicochemical attributes, pyrolysis characteristics, and kinetic behavior through thermodynamic analysis [21]. Martinez et al. (2020) conducted a study to investigate the slow pyrolysis of digested dairy cattle manure using both one-step and multi-step pyrolysis processes, spanning a temperature range from 250°C to 600°C [22]. Rumaihi et al. (2021) compared pyrolysis kinetics with gasification kinetics and found that camel dung necessitates a higher activation energy for its pyrolysis decomposition [13]. Akyürek et al. (2021) investigated the synergetic effects of co-pyrolysis of different waste feedstocks, using the Flynn-Wall-Ozawa model to determine kinetic parameters, revealing that the apparent activation energy values for the decomposition of sheep manure into a recycled polyethylene terephthalate blend for green energy production [23].

However, research conducted by Akyurek has not included kinetic analysis of pure sheep manure using the Friedman model [23]. Consequently, research on TGA of sheep manure is still limited. Therefore, in this work, kinetic and thermodynamic analysis were performed using Friedman and Coats-Redfern model on sheep manure. This research is significant for understanding the thermal behavior and degradation kinetics of animal manure biomass. The TGA method allows measuring changes in the mass of samples when heated in stages, thus providing insights into the thermal reactions that occur. Through this research, it is expected that the pyrolysis behavior and thermal characteristics of sheep manure can be beneficial for the development of sheep manure biomass processing process.

MATERIAL AND METHODS

This section describes the properties of feedstock pyrolysis and methods for analyzing reactions kinetics.

Feedstock

This study was conducted in West Java, Indonesia. The pyrolysis used sheep manure as feedstock. The sheep manure was obtained from local farms in West Java, Indonesia. Based on data from Indonesian Directorate of Livestock, Fisheries and Forestry Statistics, the sheep population has the greatest growth. The sheep population in Indonesia is experiencing positive growth, with an average annual growth rate of 0.97%, compared to other livestock populations e.g. goats, cows, horses and pigs. Thus, it can be concluded that sheep manure has a high potential for usage as renewable biomass energy. Regionally, the sheep population is clustered in Java. West Java is the province with the largest sheep population in Indonesia, with as many as 12.25 million heads. Therefore, West Java has a role in contributing almost 68.41% of the total sheep population in Indonesia [5].

Kinetic modelling

In this study, biomass analysis was carried out through Simultaneous Thermogravimetric-Differential Thermal-Differential Scanning Calorimetry Analysis (TGA-DTA-DSC) using NEXTA STA (Hitachi STA200RV with Real View Sample Observation). The inert gas used in this test is pure nitrogen. The used sample was sheep manure powder 6.790 mg. Prior to thermogravimetric testing, the sheep manure was firstly separated from soil and other impurities. Furthermore, the sheep manure was dried until it reached a mass reduction of approximately 90%. In this study, a nitrogen flow rate of 100 ml/min was used. The sample is heated at a heating rate of 10°C/min to 900°C. Thermal analysis using TGA, DTA, and DSC. TGA was used to study the degradation in mass of biomass sample as it is subjected to controlled heating. DSC measured the heat absorbed during heating in the form of energy or enthalpy, while DTA measured the difference in sample temperature and standard (inert) material.

The TGA results were analyzed using the Arrhenius equation with a one-stage global single reactions kinetics model. This model is the simplest model which assumes that the rate of decomposition depends on the order of the reaction shown in eq. (1) [8], [21], [24]. Many studies on the analysis of pyrolysis kinetics use the TGA test results. There are three types of kinetic models used for the kinetics analysis of pyrolysis of biomass e.g., differential, isoconventional (model-free), model-fitting and pseudo-component [25]–[27]. The basic equation used in all studies on kinetics is shown in eq. (1) [28]:

$$\frac{dX}{dt} = k(T)f(X) \quad (1)$$

where k is rate constant and $f(X)$ is reaction model a reaction model that describes the reaction mechanism. Conversion fraction X is shown in eq. (2) :

$$X = \frac{\text{initial sample mass} - \text{sample mass at time } t}{\text{initial sample mass} - \text{final sample mass}} \quad (2)$$

To calculate the constant k , the Arrhenius equation is used in eq. (3) :

$$k = A e^{-E/RT} \quad (3)$$

where:

A = frequency factor (s^{-1})

E = activation energy ($\frac{J}{mol}$)

R = ideal gas constant = $8.314 J \cdot mol^{-1} K^{-1}$

T = temperature (K)

Substitution of eq. (1) and eq. (3) is obtained:

$$\frac{dX}{dt} = A e^{-E/RT} f(X) \quad (4)$$

If the temperature is varied by the constant β , which is the heating rate $\beta = \frac{dT}{dt}$, β will become the Friedman Kinetic Model eq. (5) :

$$\frac{dX}{dt} = \frac{A}{\beta} e^{-E/RT} f(X) \quad (5)$$

Eq. (5) converted to logarithmic eq. (6) :

$$\ln \frac{dX}{dt} = \ln \left(\beta \frac{dX}{dT} \right) = \ln[A f(X)] - \frac{E}{RT} \quad (6)$$

If it is assumed $y = a + bx$, then:

$$y = \ln \frac{dX}{dt} \quad (7)$$

$$b = -\frac{E}{RT} \quad (8)$$

$$a = \ln[A f(X)] \quad (9)$$

To determine the activation energy, it can be started by plotting the data with y on the vertical axis and x where $x = 1/T$ on the horizontal axis. The slope of the plot yields the value of b , while the intercept provides the frequency factor, denotes as a .

To understand the kinetics of pyrolysis in sheep manure, it is necessary to carry out iso-conventional modeling, one of which is the Coats-Redfern model. First, the Friedman kinetic model focuses on the effect of heating rate on the reaction process. This is useful for understanding how the decomposition rate of a substance changes with different heating rates. This model produces kinetic parameters such as activation energy (E) and pre-exponential factor (A). On the other hand, the Coats-Redfern model provides a broader perspective by analyzing Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) data. This model considers various reaction mechanisms that may be involved in the thermal degradation process. The Coats & Redfern method falls into the single heating rate method. Only one test is needed with a certain TGA heating rate, then the kinetic parameter values can be known. The Coats & Redfern method is also called the model fitting method. In addition to the activation energy value and pre-exponential factor, the Coats-Redfern method is also used to determine the thermal decomposition pattern of a material [29]. The fundamental equation for Coats and Redfern method is given by eq. (10) [30]:

$$\ln \frac{g(X)}{T^2} = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (10)$$

where β is the heating rate, R is universal constant (0.008314 kJ/mol K) and $g(X)$ is a kinetic function of different reaction mechanism.

Thermodynamics parameters

Analysis of the thermodynamic parameters of the pyrolysis process are necessary to determine the reaction energy and stability. The calculation of these thermodynamic parameters relies on the results obtained from the reactions kinetics [21]. Rumaihi et al. derived estimates for activation energy values and applied the Kissinger equation to ascertain thermodynamic properties such as Gibbs free energy, enthalpy, and entropy [31]. Similar to the research carried out by Xiaojuan et al. on the pyrolysis of corn and cotton stalks, which calculated thermodynamic parameters [32]. There are three key thermodynamic parameters that need to be computed in the pyrolysis process: enthalpy, entropy, and Gibbs free energy. These parameters play a crucial role in understanding the energy changes and feasibility of the pyrolysis reaction. Enthalpy, entropy, and Gibbs free energy calculations can provide important information on the spontaneity and directionality of the pyrolysis reaction, which are essential in determining its viability and potential applications.

Enthalpy (H) describes the amount of heat energy released or absorbed during a pyrolysis reaction. A negative ΔH value indicates that the pyrolysis reaction released heat energy, while a positive ΔH value indicates that heat energy is absorbed during the reaction. The measurement of ΔH is crucial for understanding the thermal characteristics of the biomass pyrolysis process. In a pyrolysis system, enthalpy is defined as the energy required to increase the raw material's temperature from room temperature to the reaction temperature to convert biomass into gas, char, and liquid pyrolysis products [33]. The equation for the enthalpy change is shown in eq. (11). By accurately determining the enthalpy change, valuable insights can be gained about the energy balance and efficiency of pyrolysis processes, which are important for optimizing and designing pyrolysis system for various applications.

$$\Delta H = E - RT_p \quad (11)$$

where T_p = temperature at the peak of sample decomposition (K)

Gibbs free energy (G) shows the thermodynamic energy of a system that can be converted into work at constant T and P. The Gibbs free energy reaches its maximum value when the process is a reversible process. The equation for ΔG is shown in eq. (12).

$$\Delta G = E + RT_P \ln \left(\frac{k_B T_P}{h A} \right) \quad (12)$$

$$\Delta G = E + RT_P \ln \left(\frac{k_B T_P}{h A} \right) \text{ where:}$$

k_B = the Boltzmann constant = 1.38×10^{-23} (J/K)

h = the Planck constant = 6.63×10^{-34} (Js)

Entropy (S) is a thermodynamic parameter that measures the degree of disorder or randomness in a system. The equation for ΔS is shown in eq. (13).

$$\Delta S = \frac{\Delta H - \Delta G}{T_P} \quad (13)$$

RESULTS AND DISCUSSIONS

This section presents the findings derived from each step of the evaluation.

Sheep manure characteristics

The proximate and ultimate test results on the sheep manure sample used in this study is shown in the following table. The main characteristics of sheep manure are shown in moisture content, proximate test results (ash, volatile matter and fixed carbon) and ultimate analysis (C, H, N, O, S). Several components that can affect the yield of pyrolysis products are moisture, ash, sulphur and nitrogen [34]. Biomass that has a high moisture content requires a large input energy for the raw material pre-treatment process, especially for the raw material drying process. High ash content can increase biochar yield [35], [36] but decrease bio-oil yield [34]. High ash content in biomass can increase the selling price of fuel, while a high O/C ratio can reduce the selling price of fuel in biomass with the same ash content [34]. High volatile matter content in biomass can also reduce biochar yields [37].

Animal manure usually has a high organic content and low cellulose content due to bacterial and chemical reactivity in the digestive tract of animals. Bacteria present in the digestive tract of animals help in the decomposition of organic matter, such as food residues and other organic matter, which produces manure with a high organic matter content. The digestive process in the animal's body also involves chemical processes that can change the composition of organic matter, including cellulose, into a form that is more easily decomposed. So that animal manure contains a high organic matter content, and low cellulose levels [13]. In terms of physical and chemical properties, sheep manure contains 15.31–16.67% cellulose, 14.05–26.12% hemicellulose, 13.97–15.21% lignin and pH 6.98–8.52 [6]. Cellulose, hemicellulose and lignin are organic components found in sheep manure which determine the ratio of biomass degradation. One of them is if it has a high hemicellulose degradation ratio, it can increase biogas yield [38], while lignin is more difficult to degrade [39]. In addition to affecting the degradation ability, the content of these organic components also affects the combustion process. Biomass with a high lignin content is more suitable for direct combustion with sufficient oxygen supply, while biomass with a higher cellulose content can be more effective in direct combustion [40]. This is different from biomass derived from plant waste which has a higher lignocellulosic (lignin and cellulose) content, which is around 20–50% [41].

Comparing the results of previous studies shown in Table 1, there is a difference in the percentage of sheep manure component content but the magnitude is not significant. This difference in content is caused by several factors, namely type of feed, and environmental factors [42]. Franco et al investigated poultry manure that the environment during the experiment also influenced the results of the analysis [43]. When compared to other livestock, sheep manure has the highest fixed carbon content compared to cow, goat, poultry and pig manure, which is 13%, so it has the potential for a high HHV value [6].

Table 1. Comparison of sheep manure properties

| Properties | As-received basis [44] | As-received basis [6] | Dry basis [34] | Dry basis (Current study) |
|-----------------|---------------------------|--------------------------|-------------------|------------------------------|
| Ultimate | | | | |
| C | 49.0 ± 0.5 % | 51.33 % | 34.33 | 33.97 |
| H | 6.3 ± 0.1 % | 6.45 % | 4.96 | 4.27 |
| N | 3.3 ± 0.0 % | 2.65 % | 2.36 | 3.37 |
| O | 41.3 % | 38.81 % | 41.96 | 25.48 |
| S | - | 0.76 % | 0.31 | 0.58 |
| Cl | - | 0.61 % | - | - |
| Proximate | | | | |
| Moisture | 8.3 ± 0.5 % | 8 % | - | - |
| Volatile matter | 58.6 ± 0.7 % | 59.98 % | 68.61 | 52.85 |
| Fixed carbon | 16.8 ± 0.3 % | 12.79 % | 15.31 | 14.83 |
| Ash | 24.6 ± 0.6 | 19.23 % | 16.08 | 32.32 |

Thermal degradation analysis

Kinetic parameters on sheep manure were analyzed using TGA. The mass degradation curve of the sheep manure sample exhibits two distinct stages: dehydration and devolatilization, as depicted in the Figure 1. Dehydration involves the removal of moisture from the biomass. Prior to the pyrolysis stage, sheep manure biomass undergoes a drying and dehydration process that occurs within a temperature range of 30–140°C (Stage 1). During this stage, heat is absorbed by the sheep manure biomass for water evaporation. In the devolatilization stage (Stage 2 and Stage3), the gas components within the biomass are separated. Water and light molecules, such as CO and CO₂, are released during this stage. The devolatilization process occurs at a temperature range of 210–900°C. Specifically, Stage 2 (210–500°C) involves the decomposition of hemicellulose and cellulose, while Stage 3 (>590°C) involves the degradation of lignin. The decomposition of hemicellulose occurs at temperatures ranging from 220–300°C, cellulose decomposes at 300–340°C, and lignin degradation occurs at temperatures exceeding 340°C [13]. Ranjeet et al. have also concluded that in biomass pyrolysis in the temperature zone of 150–500 °C, the peak observed was due to the degradation of cellulose and hemicellulose compounds [45]. Figure 1 the Derivative Thermogravimetry (DTG) curve shows that the highest rate of mass decomposition occurs at temperatures of 250°C and 450°C where the devolatilization process begins to overcome the manure activation energy barrier.

In previous studies, it was reported that lignin degradation occurs at temperatures above 450°C, and the decomposition process typically exhibits a broader temperature range, spanning from 180°C to 900°C, with a lower reaction rate [41]. The decomposition curve of hemicellulose, cellulose and lignin in animal manure is influenced by the mineral content contained in animal manure, namely potassium and sodium [13]. Figure 1 Derivative Thermogravimetry (DTG) curve depicts two peaks in the volatilization area of hemicellulose and cellulose. In contrast to the research conducted by Cheng Tung Chong [13], who reported

a single peak in the DT (Derivative Thermogravimetry) curve due to the high potassium and sodium content in horse manure.

This devolatilization stage is pyrolysis in which the decomposition of biomass occurs into biochar, biogas and bio-oil products. In the sheep manure TG curve, sheep manure degrades rapidly and significantly starting at a temperature of 210°C and will gradually slow down when the temperature is above 500°C. In the sheep manure TG curve, there is a rapid and significant degradation starting at a temperature of 210°C, which gradually slows down when the temperature exceeds 500°C. After reaching 500°C, mass degradation continues to decrease steadily until it reaches 900°C. This observation suggests that most of the volatile compounds have been lost at this temperature, leaving behind a more stable and less easily decomposable material. The mineral content present in animal manure can increase the activation energy, thereby influencing the carbonization process [46].

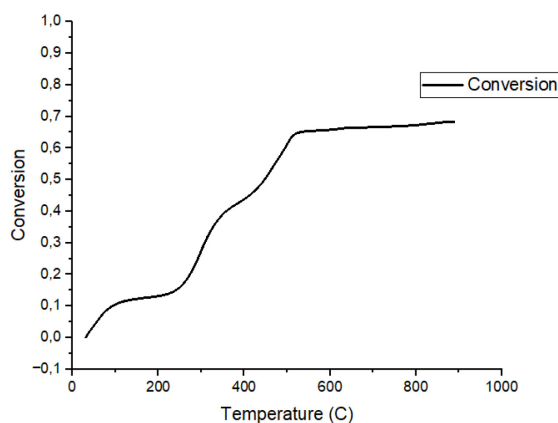


Figure 1. Conversion fraction in sheep manure vs temperature

Figure 1 depicts about 70% of sheep manure has been degraded at a temperature of 450°C. At temperatures above 450°C, lignin degradation occurs until it is converted to a temperature of 900°C. The sheep manure was not completely decomposed 100% probably due to the need for a TGA test with a heating rate above 10°C/min. The sheep manure was not completely decomposed to 100%, likely due to the requirement for a TGA test with a heating rate exceeding 10°C/min. When tested with a heating rate of 10°C/min, the decomposition of sheep manure reached only approximately 70%. A high heating rate can affect the thermal and mass degradation of the sample [13]. The ash content in sheep manure is 32.32 and this is greater than the Rabah [34] study. Ash content include calcium, potassium, and magnesium, among others. In addition, ash contains minerals; among these are calcium, potassium, and magnesium found in ash derived from poultry manure [47]. During combustion, the organic matter in the biomass is converted into gases, leaving behind the inorganic minerals as ash [48]. The ash cannot be converted into usable products or energy, and its existence complicates the conversion process. In fact, increasing ash content in biomass can decrease the volatile matter, carbon, and hydrogen contents of the biomass, thereby reducing bio-oil yield [49].

Based on the results of TGA testing on sewage sludge by Naqvi et al. [30], the acceleration of the heating rate accelerates the thermal degradation of materials at higher temperatures. This suggests that a faster increase in temperature of sewage sludge samples results in a shorter thermal delay. Additionally, a higher heating rate leads to the release of a relatively larger amount of volatile substances.

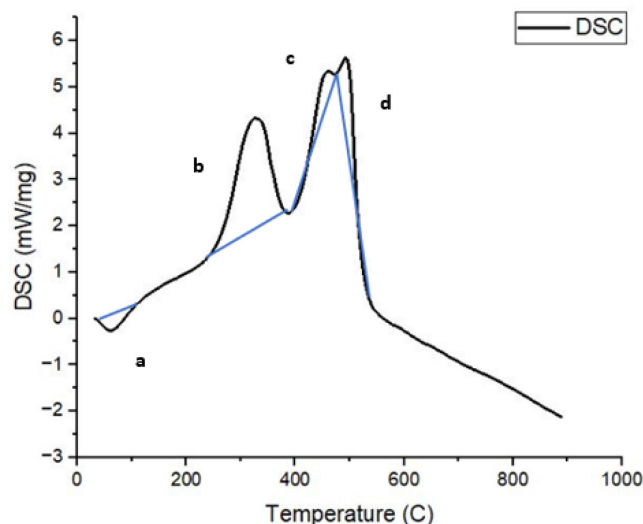


Figure 2. DSC Curve

The direction of heat flow during the pyrolysis process of sheep manure is shown in the Figure 2. Heat flow during the pyrolysis process increases with rising temperature until it reaches approximately 500°C. Beyond this temperature, the heat flow gradually decreases. Stage 1 is an endothermic reaction in which heat energy is absorbed, primarily used to evaporate the water content in the biomass. This stage also activates the pyrolysis reaction in Stage 2 by breaking the chemical bonds within the feedstock [50]. The endothermic peak in sheep manure is at 800°C in Stage 3. The heat flow value at the endothermic peak was 140 mW.s/mg. Stage 2 is dominated by exothermic reactions where heat energy is released. In an exothermic reaction, the heat flow value increases gradually. The amount of heat flow in the exothermic reaction at peaks b, c and respectively -1.00 W.s/mg, -153 mW.s/mg, 351 mW.s/mg. In DSC analysis, changes in heat flow occur when the feedstock changes temperature.

Kinetic model analysis

Thermal behaviour and reactions kinetics are very important in the analysis and development of pyrolysis process. Because it can be used to predict reaction rates, optimize experiments and determine operational parameters. In general, the kinetics of pyrolysis is stated in the Arrhenius Equation which involves activation energy, frequency factor and reaction order [51]. Son Hu et al. have also applied the Arrhenius Equation to investigate the kinetics of biomass pyrolysis using the Ozawa method [52]. When compared with other isoconventional models (Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Staring), the Friedman model is widely used. This is because the value calculated by the Friedman model is more accurate and close to the actual activation energy value in the pyrolysis process [14]. In the Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Staring models, there are approximations and assumptions, while the Friedman model is not. The results of modelling the kinetics of the sheep manure reaction are shown in Figure 3.

To calculate the value of activation energy (E) obtained from plotting data y with x. The value of E is calculated from the slope equation (b) and the value of the frequency factor (A) is obtained from the intercept (a). From the graph of the relationship between $\ln y$ and x, the R^2 value is 0.893 (89.3%). The R^2 value indicates that the linear regression model represents the variability of the data, if the R^2 value is close to 1 or 100%, the better the linear regression model and vice versa. The graph shows a fairly good R^2 , thus that the linear regression model can be used. Based on the Arrhenius equation, it is shown that the smaller the value of the frequency factor (A), the greater the activation energy (E). The frequency factor represents the magnitude of the collision that occurs between reacting molecules. Thus, if the value of the frequency factor is small, it implies that a significant activation energy is required for the

reaction to occur. In the context of this pyrolysis study, the decomposition reaction necessitates a higher activation energy when the frequency factor is smaller.

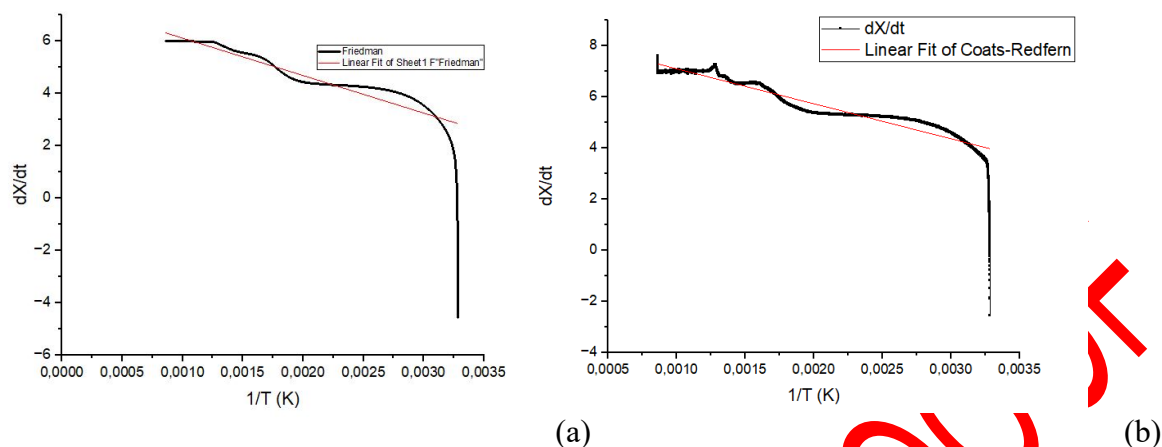


Figure 3. dX/dT vs $1/T$ curve Friedman (a) and Coats-Redfern (b)

The activation energy required in the pyrolysis process of sheep manure is shown in Figure 4. Activation energy is one of the challenges that must be completed before a chemical reaction occurs. The higher the value of the activation energy, the more complex and difficult a reaction can occur. The activation energy determines the reactivity and rate sensitivity of the reaction [53]. It is possible that the minerals in the manure act as barriers to heat diffusion and release of volatiles that are degraded in the combustion stage. Therefore, the high mineral content in animal waste causes a high activation energy requirement [14]. Overall, the average activation energy of sheep manure based on the Friedman model is 21.32 kJ/mol and Coats-Redfern is 26.20 kJ/mol.

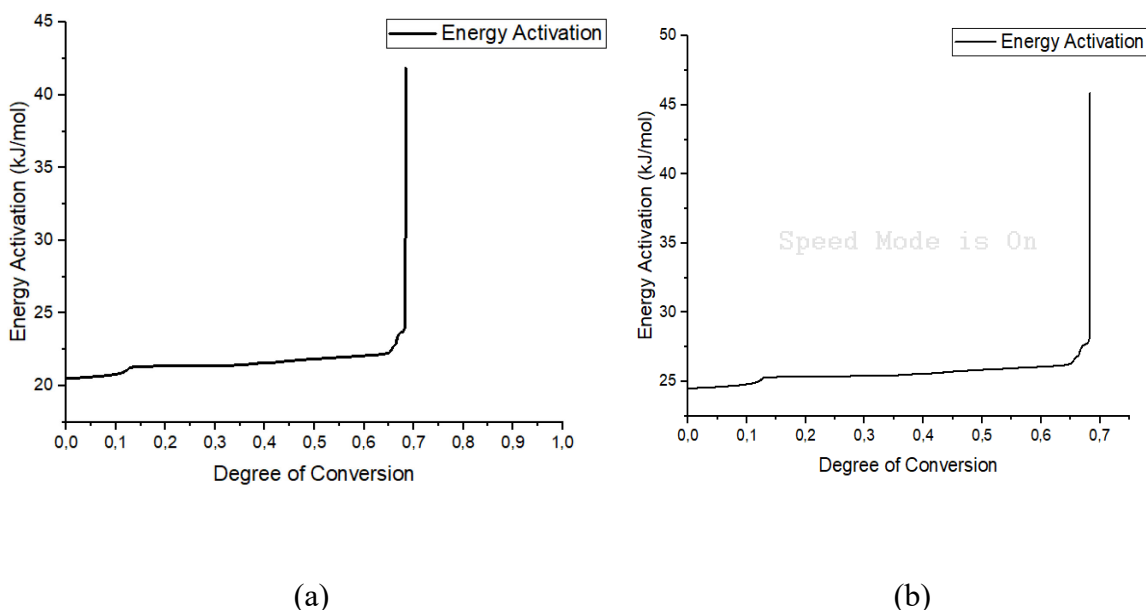


Figure 4. Activation Energy of Friedman Model (a) and Coats-Redfern (b)

The Friedman and Coats-Redfern modelling activation energy shows that the value of the activation energy during the degradation process has increased. At the beginning of the reaction (stage I) the required activation energy is still small, namely 21–22 kJ/mol for Friedman model and 24–25 kJ/mol for Coats-Redfern model. This initial reaction occurs at a temperature of 30–

140°C. This is due to the degradation of some extractives with small molecules, such as fat, ammonium, sugar, and others [54]. In stage II there is a gradual increase in energy. At this stage the required activation energy tends to be stable where decomposition of hemicellulose and cellulose occurs. At this stage an activation energy of 22–25 kJ/mol is required and for Coats-Redfern model 25–28 kJ/mol. The highest increase in activation energy occurs at the degree of conversion 0.65–0.70 which occurs in stage III. At this stage, lignin decomposition occurs at temperatures > 450°C. The activation energy required at this stage is 25–41 kJ/mol for Friedman and 28–46 kJ/mol for Coats-Redfern model, due to the structural nature and complex chemical bonds possessed by lignin. The structure of lignin is composed of a complex and diverse range of phenolic polymers, which are linked by a variety of strong chemical bonds, including aromatic bonds, ester bonds, and ether bonds. These bonds provide structural strength and resistance to lignin decomposition.

Thermodynamic properties

The results of the calculation of the thermodynamic parameters are shown in Table 2. The calculation of thermodynamic parameters uses eq. (10), (11), (13), to obtain the value of the enthalpy change, Gibbs free energy and entropy change. The value of A is calculated from the eq. (12) at the peak T of 300 °C with a heating rate of 10 °C/min. The frequency value of factor A shows the reaction that occurs. If the A value is small, namely $<10^{-9} \text{ s}^{-1}$, then the reaction that occurs is a surface reaction [55]. However, if the reaction is independent, i.e. independent of surface area, then the small frequency factor may be due to a closed junctional complex. Conversely, a high frequency factor ($\geq 10^{-9} \text{ s}^{-1}$) indicates the presence of a liberal junctional complex [16]. This interpretation relates to the concepts of surface reactions and junctional complexes. In surface reactions, the chemical reaction occurs at the surface of the material, and the low frequency factor indicates the presence of a kinetic step involving adsorption or desorption on a confined surface. Therefore, the low frequency factor indicates that there is a dominant surface reaction in the decomposition of animal manure. However, if the chemical reaction is independent of small surface area and frequency factor, this could indicate the presence of closed junctional complexes. That is, chemical reactions occur within the molecular structure or within a confined space. Closed junctional complexes can limit the access of reactant molecules and produce a low frequency factor. On the other hand, a high frequency factor may indicate the presence of liberal junctional complexes, where chemical reactions can occur with easier access to the reactant molecules. Liberal junctional complexes are generally open and allow freer interaction of the reactant molecules, which results in a higher frequency factor.

Table 2. Comparison of thermodynamic parameters in animal manure

| Manure | Process | Method | A (s^{-1}) | ΔH (kJ/mol) | ΔS (J/mol) | ΔG (kJ/mol) | Reference |
|--------|-----------|---------------|-----------------------|------------------------|-----------------------|------------------------|--------------|
| Horse | Pyrolysis | Friedman | $3.6 \cdot 10^{20}$ | 187.10 | 0.060 | 153.10 | [13] |
| Cattle | Pyrolysis | Friedman | $7.83 \cdot 10^{28}$ | 190.60 | 0.045 | 164.47 | [14] |
| Sheep | Pyrolysis | Friedman | $9.94 \cdot 10^{18}$ | 208.43 | 0.105 | 148.00 | Current work |
| Sheep | Pyrolysis | Coats-Redfern | $3.42 \cdot 10^{18}$ | 257.32 | 0,192 | 147.00 | Current work |

Activation energies differ for different kinds of biomass. An estimate of the energy needed for pyrolysis is provided by the activation energy, which also indicates the energy needed for the decomposition phase. By determining the activation energy, we can know the extent to which the pyrolysis process is influenced by temperature and can optimize the reaction conditions to achieve the desired results. Higher activation energy values might necessitate

higher temperatures or more intense reaction conditions, whereas lower values might suggest that the pyrolysis reaction proceeds more readily at a given temperature. Sheep manure has a lower activation energy than other biomass, as indicated in the accompanying Table 3. This table shows that pine wood has the lowest activation energy.

Table 3. Activation energies obtained by this study with those from literature

| Biomass | Activation Energy (kJ/mol) | Method | Reference |
|-----------------------------------|----------------------------|--|-----------|
| Cotton husk | 187.42–269.09 | Distributed Activation Energy Model (DAEM) | [56] |
| Sugarcane trash | 135.07–320.00 | DAEM | [57] |
| Municipal solid waste | 13.00–42.00 | Coats and Redfern | [58] |
| Plastic | 81.00–140.00 | Kissinger Akahira-Sunose (KAS) | [59] |
| Pine wood | 11.66–14.08 | Friedman | [60] |
| Alga <i>polysiphonia elongata</i> | 71.11–147.57 | Friedman | [61] |
| Horse manure | 200.2 | KAS | [19] |
| | 194.6 | Friedman | |
| | 199.3 | Flynn-Wall-Ozawa (FWO) | |
| Cattle manure | 129.67–348.27 | Friedman | [14] |
| | 121.73–327.19 | FWO | |
| | 119.40–332.39 | KAS | |
| Chicken manure | 112.10 | FWO | [10] |
| | 87.64–89.96 | Coats-Redfern | |
| Camel manure | 100.06–150.79 | Coats-Redfern | [16] |
| Cow manure | 140.32 | FWO | [18] |
| | 152.38 | Friedman | |
| | 138.82 | KAS | |
| Buffalo manure | 135.20 | FWO | [18] |
| | 143.33 | Friedman | |
| | 134.68 | KAS | |
| Swine manure | 184.70 | FWO | [62] |
| | 181.34 | KAS | |
| | 181.73 | Starink | |

A positive ΔH value indicates that heat energy must be supplied from an external source for the pyrolysis process to occur. In this study, pyrolysis requires additional heat to activate and continue the chemical reactions taking place in the feedstock sample. The higher the ΔH value, the greater the amount of heat energy required in the pyrolysis process. In the table all animal manure has a positive enthalpy change value indicating that the pyrolysis process requires heat to start the reaction. In a study conducted by Prakash et.al it was concluded that the ΔH values at α 0.7 and 0.8 reached the highest values. This indicates that at this conversion fraction, the pyrolysis process requires a greater amount of heat energy to continue the chemical reaction that occurs in the feedstock sample [21].

The difference between activation energy and enthalpy in sheep manure is quite large, where activation energy has a smaller value than enthalpy. This indicates that chemical reactions or thermal processes in sheep manure tend to start more easily and proceed more quickly. This can be a favourable condition for optimizing bioenergy production from sheep manure. In the pyrolysis process of sheep manure, the low activation energy allows the degradation of raw materials to start easily, so that the reaction takes place more quickly. A higher reaction speed means that more biochar or bio-oil products can be produced in a shorter time. However, based on the conversion vs temperature curve in Figure 4, the mass

decomposition of sheep manure with a heating rate of 10°C/min is only able to decompose raw materials up to 70%. Therefore, it is necessary to do a test with a heating rate above 10°C/min or it takes a longer time and a higher temperature (> 900°C) to decompose up to 80–90%.

Based on Table 2 the ΔG value for all animal wastes has a positive value. This indicates that the pyrolysis process is an endergonic reaction that requires energy to start the reaction [21]. A positive ΔG value indicates that the free energy of the system increases during the pyrolysis process. This means that pyrolysis requires external energy to overcome the activation energy barrier and start the reaction. In this case, a positive ΔG indicates that input energy from outside is required to keep the pyrolysis process running. The Gibbs free energy change also provides information about the entropy and enthalpy changes in reactions. If the Gibbs free energy change is positive with a high value, it indicates that the reaction change results in a decrease in chaos and absorption of heat energy. Gibbs energy change (ΔG) is a thermodynamic potential that reflects the balance between enthalpy (H) and entropy (S) in a system. The Gibbs energy change provides valuable information about the favourability and direction of a chemical reaction. In pyrolysis reactions, ΔG is important for understanding chemical reactions that occur, predicting reaction directions, favourability of a reaction's thermodynamics, energy changes, system stability, and thermodynamic calculations [63].

Entropy change (ΔS) can be used as an indicator to understand the level of reactivity of feedstock samples during the pyrolysis process. A high ΔS value indicates high reactivity, while a low ΔS value indicates low reactivity. A conversion fraction of 0.7 α often indicates maximum reactivity, while a conversion fraction of 0.1 α indicates low reactivity [21]. If ΔS increases, it indicates that the feedstock undergoes transformation into biochar during the pyrolysis process. Conversely, if ΔS decreases, it indicates that the amount of unreacted sample decreases during the pyrolysis process [64]. For all conversion fraction, only low entropy values were found, indicating that the pyrolysis process is close to thermodynamic equilibrium [65]. That is, the pyrolysis reaction approaches a point where there is no significant change in the entropy of the system.

CONCLUSIONS

The findings of the physicochemical, kinetic and thermodynamic studies showed that sheep manure is a valuable source of bioenergy. Sheep manure has good potential to be used as feedstock for pyrolysis because it contains the highest C and H compared to other livestock manure. TGA was conducted with heating rate 10°C/min in a temperature range of 30–900°C. Based on the TGA of sheep manure, there are stages of dehydration and devolatilization. The temperature range for the dehydration stage is 30–140°C while the devolatilization stage is 210–900°C. However, at temperatures more than 500°C, mass degradation decreases until it reaches a temperature of 900°C. However, at this temperature, volatile compounds are no longer present in the solid phase but have been released into the gas phase. The devolatilization stage includes the degradation of cellulose and hemicellulose (210–500°C), lignin (>590°C).

The analysis of pyrolysis reaction kinetics utilized the Friedman model. It resulted in an average activation energy of 21.32 kJ/mol, while the Coats-Redfern model yielded 26.20 kJ/mol. The calculated activation energy used to estimate thermodynamic parameters such as entropy, enthalpy, Gibbs free energy. The frequency factor obtained is $9.94 \cdot 10^{18}$ which indicates that the pyrolysis process of sheep manure is a complicated process. The enthalpy value of 208.43 kJ/mol indicates that pyrolysis of sheep manure. The high entropy indicates that the pyrolysis of sheep manure has high reactivity.

Based on thermodynamic analysis, the difference between activation energy and enthalpy in sheep manure is quite large, where activation energy has a smaller value than enthalpy. This indicates that chemical reactions or thermal processes in sheep manure tend to start more easily and proceed more quickly. However, according to conversion curve, the mass decomposition

of sheep manure with a heating rate of 10°C/min is only able to decompose sheep manure up to 70%. Therefore, it is necessary to do a test with a heating rate above 10°C/min or it takes a longer time and a higher temperature (> 900°C) to decompose up to 80–90%.

For further studies, it is necessary to carry out the TGA test with a higher heating rate so that pyrolysis kinetics can be analyzed in detail. This is very useful for optimizing the pyrolysis process. The study of TGA, kinetics and thermodynamics as one of the basics in the development of pyrolysis reactors starting from fabrication design and configuration.

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REFERENCES

1. B. Khoshnevisan *et al.*, “A critical review on livestock manure biorefinery technologies: Sustainability, challenges, and future perspectives,” *Renew. Sustain. Energy Rev.*, vol. 135, 2021, <https://doi.org/10.1016/j.rser.2020.110033>.
2. L. R. Amjith and B. Bavanish, “A review on biomass and wind as renewable energy for sustainable environment,” *Chemosphere*, vol. 293, no. January, p. 133579, 2022, <https://doi.org/10.1016/j.chemosphere.2022.133579>.
3. M. of E. and M. R. R. of Indonesia, “Handbook of Energy and Economic Statistics of Indonesia,” 2021. <https://www.esdm.go.id/en/publication/handbook-of-energy-economic-statistics-of-indonesia-heesi> (accessed Jul. 10, 2023).
4. A. E. Erdogan, R. Polat, and G. Ozbay, “Pyrolysis of goat manure to produce bio-oil,” *Eng. Sci. Technol. an Int. J.*, vol. 22, no. 2, pp. 452–457, 2019, <https://doi.org/10.1016/j.jestech.2018.11.007>.
5. S. Indonesia, “Livestock in Figures 2022,” 2022. <https://www.bps.go.id/en/publication/2022/06/30/4c014349ef2008bea02f4349/peterna-kan-dalam-angka-2022.html> (accessed Jul. 11, 2023).
6. P. Parthasarathy, T. Al-Ansari, H. R. Mackey, K. Sheeba Narayanan, and G. McKay, “A review on prominent animal and municipal wastes as potential feedstocks for solar pyrolysis for biochar production,” *Fuel*, vol. 316, 2022, <https://doi.org/10.1016/j.fuel.2022.123378>.
7. J. Escalante *et al.*, “Pyrolysis of lignocellulosic, algal, plastic, and other biomass wastes for biofuel production and circular bioeconomy: A review of thermogravimetric analysis (TGA) approach,” *Renew. Sustain. Energy Rev.*, vol. 169, 2022, <https://doi.org/10.1016/j.rser.2022.112914>.
8. D. Mallick *et al.*, “Mechanistic investigation of pyrolysis kinetics of water hyacinth for biofuel employing isoconversional method,” *Sustain. Energy Technol. Assessments*, vol. 57, 2023, <https://doi.org/10.1016/j.seta.2023.103175>.
9. A. M. Sokoto and T. Bhaskar, “Pyrolysis of Waste Castor Seed Cake: A Thermo-Kinetics Study,” *Eur. J. Sustain. Dev. Res.*, vol. 2, no. 2, 2018, <https://doi.org/10.20897/ejosdr/81642>.
10. Yıldız, Z., Kaya, N., Topcu, Y., & Uzun, H , “Pyrolysis and optimization of chicken manure wastes in fluidized bed reactor: CO2 capture in activated bio-chars,” *Process Safety and Environ. Protection.*, vol. 130, pp. 297-305, 2019, <https://doi.org/10.1016/j.psep.2019.08.011>.
11. M. Hu *et al.*, “Thermogravimetric kinetics of lignocellulosic biomass slow pyrolysis using distributed activation energy model, Fraser–Suzuki deconvolution, and iso-conversional method,” *Energy Convers. Manag.*, vol. 118, pp. 1–11, 2016, <https://doi.org/10.1016/j.enconman.2016.03.058>.
12. P. Basu, *Biomass Gasification and Pyrolysis Practical Design*. Kidlington, Oxford,

- OX5 1GB, UK: Academic Press, 2010.
13. C. T. Chong *et al.*, "Pyrolysis characteristics and kinetic studies of horse manure using thermogravimetric analysis," *Energy Convers. Manag.*, vol. 180, pp. 1260–1267, 2019, <https://doi.org/10.1016/j.enconman.2018.11.071>.
 14. X. Yuan, T. He, H. Cao, and Q. Yuan, "Cattle manure pyrolysis process: Kinetic and thermodynamic analysis with isoconversional methods," *Renew. Energy*, vol. 107, pp. 489–496, 2017, <https://doi.org/10.1016/j.renene.2017.02.026>.
 15. X. Pu, M. Wei, X. Chen, L. Wang, and L. Deng, "Thermal Decomposition Characteristics and Kinetic Analysis of Chicken Manure in Various Atmospheres," *Agriculture*, vol. 12, no. 5, 2022, <https://doi.org/10.3390/agriculture12050607>.
 16. P. Parthasarathy, A. Fernandez, T. Al-Ansari, H. R. Mackey, R. Rodriguez, and G. McKay, "Thermal degradation characteristics and gasification kinetics of camel manure using thermogravimetric analysis," *J. Env. Manag.*, vol. 287, p. 112345, 2021, <https://doi.org/10.1016/j.jenvman.2021.112345>.
 17. P. Parthasarathy, T. Al-Ansari, H. R. Mackey, and G. McKay, "Effect of heating rate on the pyrolysis of camel manure," *Biomass Convers. Biorefinery*, vol. 13, no. 7, pp. 6023–6035, 2021, <https://doi.org/10.1007/s13399-021-01531-9>.
 18. M. Ashraf *et al.*, "Non-isothermal thermo-kinetics and empirical modeling: Comparative pyrolysis of cow and Buffalo manure," *Therm. Sci. Eng. Prog.*, vol. 37, no. October 2022, 2023, <https://doi.org/10.1016/j.tsep.2022.101568>.
 19. Wang, H., Wang, L., Zhang, J., Jing, Y., & Cao, Y., "P Effects of pyrolysis temperature and reaction time on the performance of swine-manure-derived bio-binder," *Transportation Research Part D: Transport and Environment*, vol. 89, 2020, <https://doi.org/10.1016/j.trd.2020.102606>.
 20. M. Fernandez-Lopez, G. J. Pedrosa-Castro, J. L. Valverde, and L. Sanchez-Silva, "Kinetic analysis of manure pyrolysis and combustion processes," *Waste Manag.*, vol. 58, pp. 230–240, 2016, <https://doi.org/10.1016/j.wasman.2016.08.027>.
 21. P. Parthasarathy *et al.*, "Thermogravimetric analysis of camel dung, date stone, and their blend for pyrolytic, kinetic, and thermodynamic studies," *Clean. Chem. Eng.*, vol. 4, p. 100072, Dec. 2022, <https://doi.org/10.1016/j.clce.2022.100072>.
 22. M. Atienza-Martínez, J. Abrego, G. Gea, and F. Marías, "Pyrolysis of dairy cattle manure: evolution of char characteristics," *J. Anal. Appl. Pyrolysis*, vol. 145, p. 104724, 2020, <https://doi.org/10.1016/j.jaap.2019.104724>.
 23. Z. Akyürek, "Synergetic effects during co-pyrolysis of sheep manure and recycled polyethylene terephthalate," *Polymers (Basel)*, vol. 13, no. 14, 2021, <https://doi.org/10.3390/polym13142363>.
 24. I. Y. Mohammed, Y. A. Abakr, J. N. Xing Hui, P. A. Alaba, K. I. Morris, and M. D. Ibrahim, "Recovery of clean energy precursors from Bambara groundnut waste via pyrolysis: Kinetics, products distribution and optimisation using response surface methodology," *J. Clean. Prod.*, vol. 164, pp. 1430–1445, 2017, <https://doi.org/10.1016/j.jclepro.2017.07.068>.
 25. H. Liu, M. S. Ahmad, H. Alhumade, A. Elkamel, S. Sammak, and B. Shen, "A hybrid kinetic and optimization approach for biomass pyrolysis: The hybrid scheme of the isoconversional methods, DAEM, and a parallel-reaction mechanism," *Energy Convers. Manag.*, vol. 208, 2020, <https://doi.org/10.1016/j.enconman.2020.112531>.
 26. A. A. Jain, A. Mehra, and V. V. Ranade, "Processing of TGA data: Analysis of isoconversional and model fitting methods," *Fuel*, vol. 165, pp. 490–498, 2016, <https://doi.org/10.1016/j.fuel.2015.10.042>.
 27. P. Brachi, F. Miccio, M. Miccio, and G. Ruoppolo, "Pseudo-component thermal decomposition kinetics of tomato peels via isoconversional methods," *Fuel Process. Technol.*, vol. 154, pp. 243–250, 2016, <https://doi.org/10.1016/j.fuproc.2016.09.001>.
 28. B. Khiari and M. Jeguirim, "Pyrolysis of Grape Marc from Tunisian Wine Industry:

- Feedstock Characterization, Thermal Degradation and Kinetic Analysis,” *Energies*, vol. 11, no. 4, 2018, <https://doi.org/10.3390/en11040730>.
29. G. Chen *et al.*, “Comparison of kinetic analysis methods in thermal decomposition of cattle manure by thermogravimetric analysis,” *Bioresour. Technol.*, vol. 243, pp. 69–77, 2017, <https://doi.org/10.1016/j.biortech.2017.06.007>.
 30. S. R. Naqvi *et al.*, “Pyrolysis of high ash sewage sludge: Kinetics and thermodynamic analysis using Coats-Redfern method,” *Renew. Energy*, vol. 131, pp. 854–860, 2019, <https://doi.org/10.1016/j.renene.2018.07.094>.
 31. A. Al-Rumaihi *et al.*, “Thermal degradation characteristics and kinetic study of camel manure pyrolysis,” *J. Environ. Chem. Eng.*, vol. 9, no. 5, 2021, <https://doi.org/10.1016/j.jece.2021.106071>.
 32. X. Guo, Z. Xu, X. Zheng, X. Jin, and J. Cai, “Understanding pyrolysis mechanisms of corn and cotton stalks via kinetics and thermodynamics,” *J. Anal. Appl. Pyrolysis*, vol. 164, p. 105521, 2022, <https://doi.org/10.1016/j.jaap.2022.105521>.
 33. D. E. D. and R. C. Brown, “Enthalpy for Pyrolysis for Several Types of Biomass,” *Energy & Fuels*, vol. 17, pp. 934–939, 2003, <https://doi.org/10.1021/ef020260x>.
 34. A. A. Rabah, “Livestock manure availability and syngas production: A case of Sudan,” *Energy*, vol. 259, p. 124980, 2022, <https://doi.org/10.1016/j.energy.2022.124980>.
 35. W. Li, Q. Dang, R. C. Brown, D. Laird, and M. M. Wright, “The impacts of biomass properties on pyrolysis yields, economic and environmental performance of the pyrolysis-bioenergy-biochar platform to carbon negative energy,” *Bioresour. Technol.*, vol. 241, pp. 959–968, 2017, <https://doi.org/10.1016/j.biortech.2017.06.049>.
 36. S. Adilah, S. Nur, and A. Nurhayati, “Slow Pyrolysis of Oil Palm Empty Fruit Bunches for Biochar Production and Characterisation,” *J. Phys. Sci.*, vol. 25, no. 2, pp. 97–112, 2014, [Online]. Available: <http://jps.usm.my/wp-content/uploads/2015/06/25-2-8.pdf>.
 37. L. J. R. Nunes, J. C. De Oliveira Matias, and J. P. Da Silva Catalão, “Introduction,” in *Torrefaction of Biomass for Energy Applications*, Oxford, UK: Academic Press, 2018, pp. 1–43.
 38. M.-Q. Orlando and V.-M. Borja, “Pretreatment of Animal Manure Biomass to Improve Biogas Production: A Review,” *Energies*, vol. 13, no. 14, 2020, <https://doi.org/10.3390/en13142713>.
 39. A. Naji, S. G. Rechdaoui, E. Jabagi, C. Lacroix, S. Azimi, and V. Rocher, “Horse Manure and Lignocellulosic Biomass Characterization as Methane Production Substrates,” *Fermentation*, vol. 9, no. 6, 2023, <https://doi.org/10.3390/fermentation9060580>.
 40. Z. W. E. N. Wei Liao Sharon Hurley, Yan Liu, Chuanbin Liu, Shulin Chen, “Effects of Hemicellulose and Lignin on Enzymatic Hydrolysis of Cellulose from Dairy Manure,” *Appl. Biochem. Biotechnol.*, vol. 121-1, pp. 1017–1030, 2005, <https://doi.org/10.1385/ABAB:124:1-3:1017>.
 41. S. A. El-Sayed and M. E. Mostafa, “Kinetic Parameters Determination of Biomass Pyrolysis Fuels Using TGA and DTA Techniques,” *Waste and Biomass Valorization*, vol. 6, no. 3, pp. 401–415, 2015, <https://doi.org/10.1007/s12649-015-9354-7>.
 42. A. Tomczyk, Z. Sokołowska, and P. Boguta, “Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects,” *Rev. Environ. Sci. Bio/Technology*, vol. 19, no. 1, pp. 191–215, 2020, <https://doi.org/10.1007/s11157-020-09523-3>.
 43. F. Cotana, V. Coccia, A. Petrozzi, G. Cavalaglio, M. Gelosia, and M. C. Merico, “Energy Valorization of Poultry Manure in a Thermal Power Plant: Experimental Campaign,” *Energy Procedia*, vol. 45, pp. 315–322, 2014, <https://doi.org/10.1016/j.egypro.2014.01.034>.
 44. T. Kirch, P. R. Medwell, C. H. Birzer, and P. J. van Eyk, “Feedstock Dependence of Emissions from a Reverse-Downdraft Gasifier Cookstove,” *Energy Sustain. Dev.*, vol.

- 56, pp. 42–50, 2020, <https://doi.org/10.1016/j.esd.2020.02.008>.
45. R. K. Mishra and K. Mohanty, “Pyrolysis kinetics and thermal behavior of waste sawdust biomass using thermogravimetric analysis,” *Bioresour. Technol.*, vol. 251, pp. 63–74, 2018, <https://doi.org/10.1016/j.biortech.2017.12.029>.
 46. Y. Xu and B. Chen, “Investigation of thermodynamic parameters in the pyrolysis conversion of biomass and manure to biochars using thermogravimetric analysis,” *Bioresour. Technol.*, vol. 146, pp. 485–493, 2013, <https://doi.org/10.1016/j.biortech.2013.07.086>.
 47. M. Cempa, P. Olszewski, K. Wierzchowski, P. Kucharski, and B. Białecka, “Ash 0086from Poultry Manure Incineration as a Substitute for Phosphorus Fertiliser,” *Materials (Basel)*, vol. 15, no. 9, 2022, <https://doi.org/10.3390/ma15093023>.
 48. U. Kleinhans, C. Wieland, F. J. Frandsen, and H. Spliethoff, “Ash formation and deposition in coal and biomass fired combustion systems: Progress and challenges in the field of ash particle sticking and rebound behavior,” *Prog. energy Combust. Sci.*, vol. 68, pp. 65–168, 2018, <https://doi.org/10.1016/j.pecs.2018.02.001>.
 49. O, “Critical Analysis of Process Parameters for Bio-oil Production via Pyrolysis of Biomass: A Review,” *Recent Patents Eng.*, vol. 7, no. 2, pp. 98–114, 2013, <https://doi.org/10.2174/18722121113079990005>.
 50. M. Van de Velden, J. Baeyens, A. Brems, B. Janssens, and R. Dewil, “Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction,” *Renew. Energy*, vol. 35, no. 1, pp. 232–242, 2010, <https://doi.org/10.1016/j.renene.2009.04.019>.
 51. Q. V Bach and W. H. Chen, “Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review,” *Bioresour. Technol.*, vol. 246, pp. 88–100, 2017, <https://doi.org/10.1016/j.biortech.2017.06.087>.
 52. S. Hu, A. Jess, and M. Xu, “Kinetic study of Chinese biomass slow pyrolysis: Comparison of different kinetic models,” *Fuel*, vol. 86, no. 17–18, pp. 2778–2788, 2007, <https://doi.org/10.1016/j.fuel.2007.02.031>.
 53. A. Ounas, A. Aboulkas, K. El harfi, A. Bacaoui, and A. Yaacoubi, “Pyrolysis of olive residue and sugar cane bagasse: Non-isothermal thermogravimetric kinetic analysis,” *Bioresour. Technol.*, vol. 102, no. 24, pp. 11234–11238, 2011, <https://doi.org/https://doi.org/10.1016/j.biortech.2011.09.010>.
 54. Y. Xu and B. Chen, “Investigation of thermodynamic parameters in the pyrolysis conversion of biomass and manure to biochars using thermogravimetric analysis,” *Bioresour. Technol.*, vol. 146, pp. 485–493, 2013, <https://doi.org/10.1016/j.biortech.2013.07.086>.
 55. A. A. D. Maia and L. C. de Moraes, “Kinetic parameters of red pepper waste as biomass to solid biofuel,” *Bioresour. Technol.*, vol. 204, pp. 157–163, 2016, <https://doi.org/https://doi.org/10.1016/j.biortech.2015.12.055>.
 56. A. Bhavanani and R. C. Sastry, “Kinetic study of solid waste pyrolysis using distributed activation energy model,” *Bioresour. Technol.*, vol. 178, pp. 126–131, 2015, <https://doi.org/10.1016/j.biortech.2014.10.028>.
 57. N. Sonoyama and J. I. Hayashi, “Characterisation of coal and biomass based on kinetic parameter distributions for pyrolysis,” *Fuel*, vol. 114, pp. 206–215, 2013, <https://doi.org/10.1016/j.fuel.2012.04.023>.
 58. I. Boumanchar et al., “Investigation of (co)-combustion kinetics of biomass, coal and municipal solid wastes,” *Waste Manag.*, vol. 97, pp. 10–18, 2019, <https://doi.org/10.1016/j.wasman.2019.07.033>.
 59. P. Tripathi and L. Rao, “Pyrolysis and combustion kinetics of refuse derived fuel having different plastic ratio,” *Bioresour. Technol. Reports*, vol. 23, 2023, <https://doi.org/10.1016/j.biteb.2023.101559>.
 60. R. Ochieng, A. L. Cerón, A. Konist, and S. Sarker, “A combined analysis of the drying and decomposition kinetics of wood pyrolysis using non-isothermal thermogravimetric

- methods,” *Energy Convers. Manag. X*, vol. 20, no. March, 2023, <https://doi.org/10.1016/j.ecmx.2023.100424>.
61. S. Ceylan, Y. Topcu, and Z. Ceylan, “Thermal behaviour and kinetics of alga *Polysiphonia elongata* biomass during pyrolysis,” *Bioresour. Technol.*, vol. 171, no. 1, pp. 193–198, 2014, <https://doi.org/10.1016/j.biortech.2014.08.064>.
62. M. Hu, K. Guo, H. Zhou, F. Shen, W. Zhu, and L. Dai, “Insights into the kinetics, thermodynamics and evolved gases for the pyrolysis of freshly excreted and solid-liquid separated swine manures,” *Energy*, vol. 288, p. 129855, 2024, <https://doi.org/10.1016/j.energy.2023.129855>.
63. I. Ali *et al.*, “Kinetic and thermodynamic analyses of dried oily sludge pyrolysis,” *J. Energy Inst.*, vol. 95, pp. 30–40, 2021, <https://doi.org/10.1016/j.joei.2020.12.002>.
64. V. Dhyani and T. Bhaskar, “Chapter 2 - Kinetic Analysis of Biomass Pyrolysis,” in *Waste Biorefinery*, T. Bhaskar, A. Pandey, S. V. Mohan, D.-J. Lee, and S. K. Khanal, Eds. Elsevier, 2018, pp. 39–83.
65. E. Müsellim, M. H. Tahir, M. S. Ahmad, and S. Ceylan, “Thermokinetic and TG/DSC-FTIR study of pea waste biomass pyrolysis,” *Appl. Therm. Eng.*, vol. 137, pp. 54–61, Jun. 2018, <https://doi.org/10.1016/j.applthermaleng.2018.03.050>.

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