

# Kinetic and Thermodynamic Analysis of Chicken Manure Pyrolysis for Sustainable Waste Management in the Poultry Industry

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## Abstract

This study explores the kinetics of the pyrolysis process applied to chicken manure as an environmentally sustainable waste management technique within the poultry industry. Pyrolysis, a thermochemical conversion method, involves the decomposition of organic materials in the absence of oxygen, yielding biochar, gases, and bio-oil. Experimental runs were conducted using a fixed-bed reactor, varying reactor temperature and heating rate settings. Pyrolytic conversion was determined by weighing the reactor contents before and after each run, allowing for the construction of pyrolytic conversion curves. Through the application of the Coats-Redfern method, the pyrolysis kinetics was determined. It was found that a second-order kinetics model exhibited better agreement with the experimental data than a first-order model, yielding coefficient of determination ( $R^2$ ) values ranging from 0.99 to 1.00, compared to 0.94 to 0.97 for the first-order model. The apparent activation energy ( $E_a$ ) was estimated to fall within the range of 140.4 to 151.2 kJ/mol. Additionally, the pre-exponential factors ( $A$ ) were found to be significantly high, on the order of  $10^{10} \text{ min}^{-1}$ , suggesting a low pyrolytic reactivity. The calculated enthalpy of reaction ( $\Delta H$ ) ranged from 134.1 to 145 kJ/mol. Importantly, the energy barrier, represented by the difference between activation energy ( $E_a$ ) and enthalpy of reaction ( $\Delta H$ ), was determined to be low at 7 kJ/mol. These findings indicate the potential for efficiently and sustainably valorizing chicken waste through pyrolysis. The outcomes of this study provide valuable insights into the kinetics and thermodynamics of chicken manure pyrolysis, supporting its adoption as an energy-efficient and environmentally sound waste management strategy within the poultry industry.

**Keywords:** Activation energy, chicken waste, Coats-Redfern, pyrolysis, waste valorisation.

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## INTRODUCTION

The utilization of chicken manure as a fertilizer has long been a common agricultural practice. However, recent research has highlighted the potential for valorizing chicken manure through pyrolysis, a thermal decomposition process (Kim *et al.*, 2008; Sikder & Joardar, 2019; Zhao *et al.*, 2020). Pyrolysis offers a means of converting chicken manure into syngas, valuable chemicals, and liquid fuels, while also producing solid char that can serve as a fertilizer. Among the pyrolysis processes, slow pyrolysis is commonly employed due to its simplicity, although fast pyrolysis shows promise for achieving higher biofuel yields. To strike a balance between liquid product yield and manageable process rates, intermediate pyrolysis

techniques involving rotary kilns and auger screws are being investigated (Nyoni & Hlangothi, 2023). In the study conducted by Pandey *et al.*, (2019), the pyrolysis of chicken waste in a fluidized bed reactor resulted in a bio-oil yield of approximately 27% and a gross calorific value of 32.2 MJ/kg for the bio-oil. The solid char produced through pyrolysis can be utilized as a fertilizer to enhance soil quality in agricultural lands. Sikder and Joardar (2019) compared the efficacy of poultry litter and its char as fertilizers for *Gima Kalmi* plants, observing a significant increase in plant growth and biomass production when either poultry litter or its char was applied as fertilizer. Notably, the growth enhancement was more pronounced when poultry char was utilized. However, Steiner *et al.*, (2018) argued that

the nitrogen present in poultry chars may not be readily available for plant growth, suggesting that such chars should be employed selectively, particularly in situations where nitrogen immobilization is the primary objective.

Pyrolysis is a thermal decomposition process that occurs in the absence of oxygen, resulting in the release of vapors and the formation of a solid char residue. Pyrolysis systems typically include vapor condensation units to capture condensable vapors. Various types of pyrolysis processes exist, primarily distinguished by the rate of solid heating and other operational parameters such as solid and vapor residence times. Slow pyrolysis, characterized by heating rates ranging from 0.1 to 2 °C/s, is the most commonly employed method for biomass valorization due to its simplicity (Bridgwater *et al.*, 2007; Kirtania & Bhattacharya, 2013; Chaiwong *et al.*, 2013). However, studies have demonstrated the potential of fast pyrolysis for achieving higher yields of biofuels within shorter timeframes (Bridgwater *et al.*, 2007; Bridgwater, 2013). Nevertheless, the widespread commercial adoption of fast pyrolysis processes is constrained by operational limitations. Fast pyrolysis processes typically utilize heating rates ranging from 20 to 1000 °C/s (Bridgwater *et al.*, 2007; Demirbas, 2009; Bridgwater, 2013). To overcome the challenges associated with fast pyrolysis while still attaining a significantly high yield of liquid products, researchers have turned their attention to intermediate pyrolysis processes.

Several methods of studying pyrolysis kinetics have been postulated by different researchers. The methods are classified as model-fitting and model-free methods. In model-fitting methods, different types of kinetic models are fitted into experimental data until the best statistical fit is obtained. Kinetic parameters are then calculated based on the best fit model. For this reason, in this work, the Coats-Redfern model-fitting method was used for the determination of kinetic parameters from conversion data that was generated from a bench reactor that was operated at three heating rates of 10, 15 and 25 °C/min. Furthermore, thermodynamic parameters were estimated from kinetic data that was obtained.

The thermal decomposition step lies at the core of any valorization process employing pyrolysis technology. This study aims to investigate the kinetics and thermodynamics of the thermal decomposition of chicken manure through pyrolysis. Although there is limited literature on the kinetics of chicken waste pyrolysis, various methods, including model-fitting and model-free approaches, can be employed to estimate kinetic parameters. Kim and Agblevor (2007) conducted a study on the pyrolysis kinetics of chicken litter using a thermogravimetric analyzer. Their research revealed that the apparent activation energy for the pyrolysis process ranged from 99 to 484 kJ/mol for

conversion range of 60– 80%. The Coats-Redfern method is the most popular model-fitting technique. Several methods have been proposed by different researchers to investigate pyrolysis kinetics, categorized as either model-fitting or model-free methods. In model-fitting methods, various kinetic models are fitted to experimental data to obtain the best statistical fit, and kinetic parameters are then calculated based on the optimal model. In contrast, model-free methods allow the estimation of kinetic parameters without a priori knowledge of the kinetic model by utilizing heating curves generated at different heating rates (Mishra & Mohanty, 2018). Common examples of model-free methods include the Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW), Friedman, Starink, and Distributed Activation Energy Model (DAEM). Model-free methods are conceptually simple and offer potential for estimating kinetic parameters in complex reaction systems by employing the iso-conversional principle. Activation energy and pre-exponential factors are determined through linear correlation (Trinh *et al.*, 2023). However, many model-free methods are sensitive to the accuracy and precision of the analytical techniques employed. Therefore, in this study, the Coats-Redfern model-fitting method was utilized to determine kinetic parameters based on conversion data obtained from a bench reactor operated at heating rates of 10, 15, and 25 °C/min. Additionally, thermodynamic parameters were estimated from the kinetic data obtained.

Most studies on kinetics of biomass materials have reported data generated from analytical instruments such as thermogravimetric analysers. However, in this work there is an opportunity of presenting unique findings that have not been presented elsewhere because the data analysed is extracted from a bench-scale reactor which is a much closer approximation to the practical state of things.

## MATERIALS AND METHODS

### Sample Collection and Preparation

Chicken manure was obtained from a poultry project located in Colleen Bawn, Matebele land South province of Zimbabwe. Feathers, hay, and other bedding materials were carefully removed from the manure samples. The samples had a significantly high moisture content varying from 25 to 35 %, as such, all samples were air dried in an oven for 24 hours before being used for experiments.

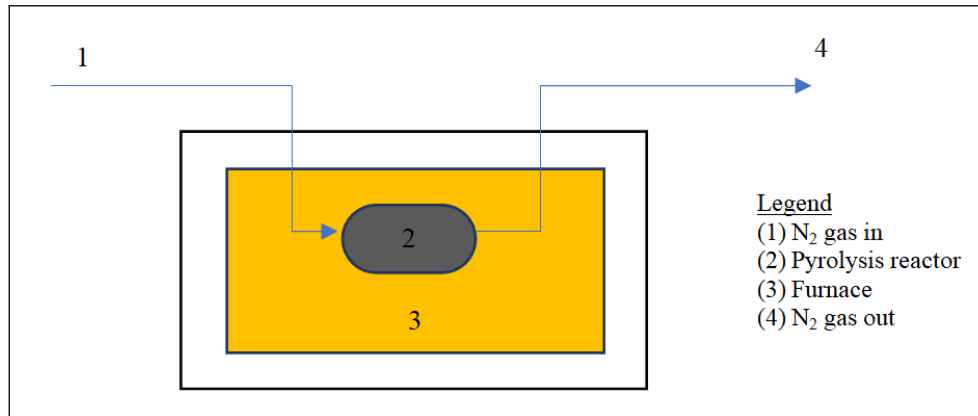
### Proximate Analysis

The analysis of moisture, volatile matter, ash and fixed carbon content of chicken manure and the char produced after pyrolysis was performed. The analysis was done according to European standard methods BS EN 14774-1:2009, BS EN 15148:2009 and BS EN 14775:2009 as outlined in the work of Liu (2011).

## Pyrolysis Experiments

Approximately 50 g of chicken manure was loaded into a cylindrical mild steel reactor of size 50 mm diameter and 100 mm long. The reactor was heated from room temperature to the desired temperature at a fixed heating rate by use of a programmable furnace. The heating was stopped as soon as the desired

temperature was attained. At the end of the pyrolysis experiment, the char remaining in the reactor was weighed. The reactor had provisions for pushing nitrogen gas in and out. Therefore, experiments were performed under inert atmosphere by maintaining nitrogen gas flow at a rate of 2 l/min through the reactor system. The experimental setup is shown in Fig. 1.



**Figure 1: Experimental set-up for pyrolysis of chicken waste in a fixed-bed reactor**

## Analysis of Data

The pyrolytic conversions ( $Y$ ) for each reactor temperature setting were determined by weighing and calculation using Eq. 1. All experiments were done in triplicates, average values of the calculated conversions were used for plots.

$$Y = \frac{w_i - w}{w_i - w_f} \quad (1)$$

The pyrolytic decomposition of chicken waste in the reactor can be modelled as a function of conversion as follows.

$$\frac{dY}{dt} = kF(Y) \quad (2)$$

The conversion function can be written as follows.

$$F(Y) = (1 - Y)^n \quad (3)$$

By substituting Eq. (3) and the general form of the Arrhenius equation into Eq. (2), we obtain

$$\frac{dY}{dt} = A \exp\left(\frac{-E_a}{RT}\right) (1 - Y)^n \quad (4)$$

If the reactor heating rate  $\beta$  ( $^{\circ}\text{C}/\text{min}$ ), given by Eq. (5) is constant, we can make use Eq. (4) to obtain Eq. (6).

$$\beta = \frac{dT}{dt} \quad (5)$$

$$\frac{dY}{dT} = \left(\frac{A}{\beta}\right) \exp\left(\frac{-E_a}{RT}\right) (1 - Y)^n \quad (6)$$

The Coats-Redfern method is a model-fitting that requires the integration of Eq. (6). As a result, we obtain the following expressions in Eqs. (7) and (8), for  $n = 1$  and  $n = 2$ , respectively.

$$\ln \left[ \frac{-\ln(1-Y)}{T^2} \right] = \ln \frac{AR}{\beta E_a} \left[ 1 - \frac{2RT}{E} \right] - \frac{E_a}{RT} \quad (7)$$

$$\ln \left[ \frac{(1-Y)^{-1} - 1}{T^2} \right] = \ln \frac{AR}{\beta E_a} \left[ 1 - \frac{2RT}{E} \right] - \frac{E_a}{RT} \quad (8)$$

where  $T$  is the absolute temperature (K),  $A$  is the pre-exponent factor in the Arrhenius equation,  $R$  is the universal gas constant ( $0.0083 \text{ kJ}/\text{mol}\cdot^{\circ}\text{C}$ ) and  $E_a$  is the activation energy ( $\text{kJ}/\text{mol}$ ).

Generally, pyrolysis activation energies are large, the first term on the right-hand side of Eqs. 7 and 8 can be regarded as a constant because the value of  $\frac{2RT}{E_a}$  can be negligible (Nyoni *et al.*, 2020). The pyrolysis kinetic parameters, that is, the activation energy and the pre-exponential factor can then be evaluated by linearising Eqs. 7 and 8 and determining the slope and y-intercept of the resultant plots. Furthermore, the rate constant ( $k$ ) can be calculated by Eq. 9. In this case,  $T$  is taken as the median value of the selected temperature range.

$$k = A \cdot e^{\frac{-E_a}{RT}} \quad (9)$$

The thermodynamic parameters can be evaluated with knowledge of kinetic parameters e.g., the enthalpy ( $\Delta H$ ), Gibbs free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) according to the following equations (Nyombi *et al.*, 2018).

$$\Delta H = E_a - RT \quad (10)$$

$$\Delta G = E_a + RT \cdot \ln \left( \frac{k_b T}{hA} \right) \quad (11)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (12)$$

where  $k_b$  and  $h$  are the Boltzmann and Planck constants, respectively.

## RESULTS AND DISCUSSION

### Proximate Analysis

Results of proximate analysis experiments are shown in Table 1. Generally, poultry waste has high moisture content as evidenced by the results of this

work and past literature (Kim & Agblevor, 2007; Kim *et al.*, 2009; Agblevor *et al.*, 2010). However, other proximate properties are highly dependent on the chicken feeding regime. For example, chicken manure used in the work of Agblevor *et al.*, (2010) had ash assay values of 21.2 % and less whereas the one reported in this work is significantly higher (27.0 %).

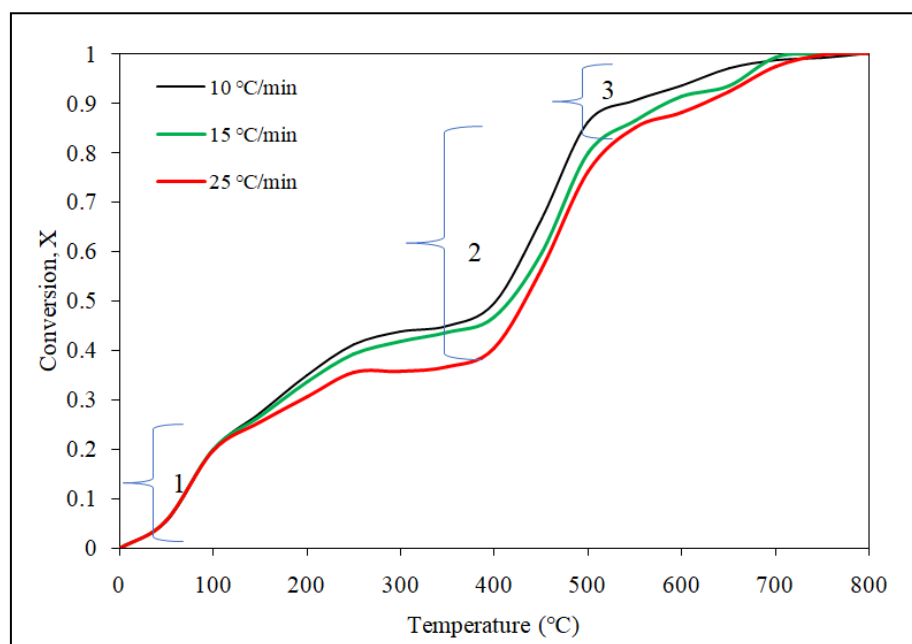
**Table 1: Proximate analysis of chicken waste**

Property	Mass (%)
Moisture (as received basis)	33.9 ± 2.46
Moisture (air dried basis)	8.1 ± 0.79
Volatiles (dry basis)	24.9 ± 1.22
Fixed carbon (dry basis)	48.1 ± 1.88
Ash (dry basis)	27.0 ± 1.88

### Mass-Loss and Conversion

The pyrolysis behaviour of chicken waste in a fixed-bed reactor can be understood by plotting the mass-loss or pyrolytic conversion against temperature; the conversion curves are presented in Fig. 2. From the three curves, it is clear that the thermal decomposition

of chicken waste in the reactor conditions used proceeds in three stages (as highlighted on the curve). Stage 1 is the dehydration stage where free and bound moisture is removed from the surface and pores of the biomass material. This process occurs in the approximate temperature range 0 – 200 °C. Also, in this temperature range, biodegradable materials i.e., low molecular weight gases and solvents are driven out (Naqvi *et al.*, 2019). Approximately, 25 – 30 % of the pyrolysable material is converted to vapour. Stage 2 is the main pyrolysis stage whereby proteins, cellulosic matter (carbohydrates and polysaccharides) and some portions of lignin decompose in the approximate temperature range of 400 – 560 °C. Approximately 50 – 55 % of the pyrolysable material is removed. Stage 3 is the pyrolysis stage whereby residual lignin and char decomposes slowly at higher temperatures (> 550 °C). Lignin is known to decompose over a wide temperature range of 200 – 600 °C (Vamvuka *et al.*, 2003; Kawamoto, 2017).



**Figure 2: Conversion curves for the pyrolysis of chicken waste in a fixed bed reactor at different heating rates**

### Kinetics Analysis

Kinetics analysis was performed for the data pertaining to the main pyrolysis stage which occurs in the temperature range 400 – 560 °C. The temperature range corresponds to the pyrolytic conversion (Y-axis) range of 0.49 – 0.9, 0.47 – 0.86 and 0.40 – 0.85 for 10, 15 and 25 °C/min. The apparent activation energies ( $E$ ) and other kinetic parameters that were derived from plots of Eqs. 7 and 8, and the use of Eq. 9 are given in Table 2. The data fits 2<sup>nd</sup> order kinetics because of the high  $R^2$  values that were obtained. As such, if it is assumed that the pyrolysis process follows 2<sup>nd</sup> order kinetics, the activation energy is in the range of 141.4 – 151.2 kJ/mol, pre-exponential factor in the range 0.38 – 4.0 x

$10^{10} \text{ min}^{-1}$  and rate constant 0.50 – 1.299  $\text{min}^{-1}$ . Interestingly, it has been found that most values of pre-exponential factor for solid-state reactions are in the range of  $10^6$  to  $10^{20} \text{ min}^{-1}$  for 1<sup>st</sup> order reactions (Nyombi *et al.*, 2013; Dubey *et al.*, 2022). Generally, low values of the pre-exponential factor (less than  $10^{10} \text{ min}^{-1}$ ) indicate the prevalence of surface reactions and a faster decomposition process (Vlaev *et al.*, 2008; Nyombi *et al.*, 2013; Dubey *et al.*, 2022). However, this is not the case with the results given in Table 2. These findings are in agreement with the works of Kim and Agblevor (2007) who reported pre-exponential factors of  $10^{11}$  –  $10^{12} \text{ min}^{-1}$  and  $10^{12}$  –  $10^{17} \text{ min}^{-1}$  for the pyrolysis of flock and broiler litter, respectively.

**Table 2: Kinetic parameters for pyrolysis of chicken waste**

Heating rate (°C/min)	First order kinetics				Second order kinetics			
	$E_a$ (kJ/mol)	$A$ (min <sup>-1</sup> )	$k$ (min <sup>-1</sup> )	$R^2$	$E_a$ (kJ/mol)	$A$ (min <sup>-1</sup> )	$k$ (min <sup>-1</sup> )	$R^2$
10	90.6	2.9E+ 5	0.149	0.941	141.4	3.8E+ 9	0.590	0.989
15	98.9	1.3E +5	0.184	0.968	140.4	2.9E+ 9	0.540	0.992
25	99.4	2.8E +5	0.358	0.956	151.2	4.0E+ 10	1.299	1.000

### Thermodynamics Analysis

Knowledge of thermodynamic parameters of a process is essential in determining the viability of thermal and energy processes. Insights on aspects such as energy requirement, energy barrier and thermodynamic equilibrium can be obtained from kinetics and thermodynamics analysis. Eqs. 10, 11 and 12 enabled the calculation of the enthalpy ( $\Delta H$ ), Gibbs free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ). It can be seen from the results given in Table 3, assuming that the pyrolysis process follows 2<sup>nd</sup> order kinetics, the enthalpy of pyrolysis reaction is in the range 134.1 – 145 kJ/mol. Therefore, the pyrolysis process is endothermic; an external energy source is needed to drive the process. The difference between activation energy and enthalpy (heat of reaction) is indicative of the potential energy barrier. For the three heating rates, the difference between activation energy and enthalpy was less than 7

kJ/mol, this small difference indicates that the favourable conditions for shifting pyrolysis reactions towards the formation of stable products, therefore, the pyrolysis of chicken waste can be performed in an energy efficient manner. Entropy is dependent on the enthalpy and the Gibbs free energy. Positive entropy values imply that the orderliness of the products is less than that of reactants whilst negative entropy values indicate otherwise. In this case, the entropy values given in Table 3 are all negative indicating that the final products could have been more ordered than the initial reactants. Furthermore, a negative entropy value indicates that the activated complex that forms after heating requires a high degree of molecular arrangements within the materials structure, therefore, the pyrolysis reactivity is low and takes more time to form an activated complex.

**Table 3: Thermodynamic parameters for pyrolysis of chicken waste**

Heating rate (°C/min)	First order kinetics			Second order kinetics		
	$\Delta H$ (kJ/mol)	$\Delta G$ (kJ/mol)	$\Delta S$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta G$ (kJ/mol)	$\Delta S$ (kJ/mol)
10	84.4	253.4	-0.22	135.1	244.8	-0.15
15	92.6	252.9	-0.21	134.1	245.3	-0.15
25	93.2	247.9	-0.21	145.0	239.8	-0.13

### CONCLUSION

This paper presented kinetics and thermodynamics analyses of the pyrolysis process for chicken waste using a bench-scale fixed-bed reactor. The pyrolysis process was better fitted to 2<sup>nd</sup> order reaction kinetics with activation energy range of 140.4 – 151.2 kJ/mol. Most importantly, the analyses indicated that there is potential of performing pyrolysis of chicken waste at an energy efficient and sustainable manner. This was evidenced by the calculated low energy barrier (< 7 kJ/mol) and negative entropy values. Since most farms and industrial establishments are moving towards the attainment of energy efficient and sustainable practices, this information will be vital in the design of pyrolytic valorisation equipment and processes for chicken waste.

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