

Kinetic Study of Horse Manure through Thermogravimetric Analysis

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Horse manure contains potential source of bioenergy that can be pyrolysed to obtain bio-oil and synthesis gas. In the present work, horse manure samples collected from the horse stable in Universiti Teknologi Malaysia were analysed through thermogravimetric analysis (TGA) to determine the Arrhenius parameters and thermodynamics properties. TGA was conducted on the horse manure at heating rates of 1, 2, 5, 10 °C/min in a nitrogen-filled reactor. The TGA data was analysed by using three different model-free, non-isothermal methods, namely Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Kissinger methods. Result shows the temperature for highest conversion of horse manure is within the range of 290.2-329.6 K. The Kissinger method shows the overall average activation energy of 148.47 kJ/mol, whereas FWO and KAS methods show the activation energy at different conversional fractions throughout the process with the range of 176.2-293.6 kJ/mol and 175.6-300.1 kJ/mol. Thermodynamic properties including the pre-exponential factor, enthalpy change, free Gibbs energy and entropy of horse manure during pyrolysis were also determined.

1. Introduction

Animal manure from living organisms possesses energy that can be retrieved through thermochemical process. Typically, manure usually ends up in landfill or as fertilizers. However, as stricter regulation is being imposed to prevent land and water pollutions, alternative method for disposal of animal manure is needed (Ro et al., 2007). Pyrolysis is a process capable of producing valuable char, liquid and gaseous products (Ng et al., 2017), while providing an alternative solution for landfilling and lowering greenhouse gases emission compared to other thermochemical conversion processes. Pyrolysis emits lower CO_x, SO_x and NO_x when compared to combustion and gasification (Cao et al., 2014). To design and optimize a reactor capable of pyrolysing manure, a clear insight into the pyrolysis process is needed to provide information on the reaction mechanism (Perondi et al., 2016). Further, setting up a thermochemical operational system requires data about kinetic properties that describe the sample degradation behavior during pyrolysis.

Thermogravimetric analysis is a common approach used to investigate the weight loss of sample as a function of temperature (Balasundram et al., 2017) to determine the Arrhenius parameters and describe the kinetic mechanism during pyrolysis process (Foltin et al., 2017). Model-free method enables the determination of activation energy and pre-exponential value without considering the type of kinetic model. From literature, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) are shown to be good methods in predicting kinetics at high conversional level (Foltin et al., 2017). The methods produced relatively accurate result compared to the

Advanced Kinetics and Technology Solution (AKTS) software using the ASTM E698 method (Abd-Elghany et al., 2016).

Previously, kinetic studies on manure pyrolysis have been performed on cattle ($E = 129.67\text{-}348.27$ kJ/mol) (Yuan et al., 2017), chicken ($E = 61\text{-}134$ kJ/mol) (Perondi et al., 2016) and swine ($E = 61\text{-}260$ kJ/mol) (Sharara and Sadaka, 2014), but horse manure data is not available. Some valorization processes performed using horse manure were anaerobic digestion (Hadin and Ola Eriksson, 2016), gasification (Nanda et al., 2016) and carbonization (Tsai et al., 2015). The lack of pyrolysis study is attributed to the absence of information on the kinetic properties of horse manure. Hence, this study focuses on the investigation of the kinetic and thermodynamic properties of horse manure pyrolysis using TGA. The data obtained is evaluated using model-free methods of FWO, KAS and Kissinger. The kinetic parameters are evaluated through comparison of different applied methods and correlation coefficient values.

2. Material and methods

2.1 Feedstock preparation and characterization

In this study, fresh horse manure was collected from the stable in Universiti Teknologi Malaysia, Skudai, Johor Bahru Malaysia. The sample was dried in a furnace at 120 °C for 24 hours to remove moisture. The dried horse manure was then grinded into powdery form. Characterization of horse manure was performed via ultimate and proximate analyses. Ultimate analysis was conducted using an elemental analyser (varioMICRO) to obtain the proportion of carbon, hydrogen, nitrogen and sulphur, while the oxygen portion was obtained through the difference. Proximate analysis was performed to determine the volatile matter, moisture and ash content through a thermogravimetric analyser (TGA Q500 V20.13 Build 39). Fixed carbon percentage was calculated by subtraction from the three elements obtained through proximate analysis. The gross calorific value of sample was obtained through a bomb calorimeter (IKA C2000 basic).

2.2 Method

TGA was used to conduct thermal degradation of horse manure based on the experimental procedure of ASTM E1641-16. A sample of 2 ± 1 mg of manure was weighted and placed on the holder for analysis. Prior to the test, the chamber was purged by pure nitrogen gas to ensure inert condition for pyrolysis. The sample, placed on a platinum holder was heated from room temperature to 900 °C with nitrogen carrier gas flow of 20 mL/min at the heating rate β of 1 , 2 , 5 and 10 °C/min. The weight loss and temperature change was recorded in thermogravimetric (TG) and derivative thermogravimetric (DTG) format.

2.3 Model free

Model free method allows the estimation of kinetic parameters of activation energy (E_a) and pre-exponential factor (A) which are independent of its reaction model. Thermal degradation of sample feedstock was conducted at various heating rate. The rate of conversion for feedstock, α which is dependent on temperature is expressed in Eq(1):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Three model-free methods were used for determining the E_a and A from the TGA data, namely Kissinger, Flynn-Wall-Ozawa (FWO), and Kissinger-Akahira-Sunose (KAS). Linear regression graphs can be plotted for evaluation of activation energy and pre-exponential factor from its gradient and y-intercept.

For Kissinger method, the activation energy can be calculated from the gradient of graph which is equals to $-E_a/R$ as shown in Eq(2).

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{A_\alpha R}{E}\right) - \frac{E_\alpha}{RT_p} \quad (2)$$

For FWO method, Doyle's approximation is implemented to the temperature integral, while the activation energy is calculated from the slope $-1.052(E_a/R)$ as shown in Eq(3).

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E_\alpha}{RT_{ai}} \quad (3)$$

For KAS method, the activation energy is calculated from slope $-E_a/R$ as shown in Eq(4).

$$\ln\left(\frac{\beta_i}{T_{ai}^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_{ai}} \quad (4)$$

β represent heating rate, T_p represent peak temperature, A_α represent activation energy, R represent gas constant, E_α represent activation energy, T_α represent temperature at conversion level and $g(\alpha)$ is a function that evaluates the solid-state kinetics which depends on the decomposition mechanism at any conversion degree.

2.4 Thermodynamic parameters

The thermodynamic parameters of the sample including the pre-exponential factor (A), changes of enthalpy (ΔH), free Gibbs energy (ΔG) and entropy (ΔS) are calculated using the following equations in Table 1.

Table 1: Thermodynamic parameters equation (Kim et al., 2010).

Thermodynamic Parameters	Equation
Pre-Exponential Factor, A	$A = \beta * E_\alpha * \exp\left(\frac{E_\alpha}{R * T_p}\right) / (R * T_p^2)$
Changes of Enthalpy, ΔH	$\Delta H = E_\alpha - RT$
Free Gibbs Energy, ΔG	$\Delta G = E_\alpha + R * T_p * \ln\left(\frac{K_B T_p}{h * A}\right)$
Entropy, ΔS	$\Delta S = \frac{\Delta H - \Delta G}{T_p}$

K_B is the Boltzman constant ($1.281 \times 10^{-23} \text{J/K}$), h is Plank constant ($6.626 \times 10^{-34} \text{Js}$), T_p is the DTG peak temperature, and T is the temperature at the conversion degree, α .

3. Result and discussion

3.1 Feedstock physiochemical properties

Physiochemical properties of the horse manure obtained through proximate and ultimate analysis are shown in Table 2 in wt% dry basis. The high oxygen content explains the low heating value for horse manure (17.44 MJ/kg) which is comparable to the data reported by Nanda et al. (2016). The low percentage of nitrogen and sulphur in the manure favors the production of bio-oil and syngas (Friedl et al., 2005). The content of moisture, volatile, fixed carbon and ash in the manure provides information on the end-products that could be derived during pyrolysis. The determined gross calorific value for horse manure is 17.44 MJ/kg.

Table 2: Physiochemical properties of horse manure sample

Ultimate Analysis (wt%)		Proximate Analysis (wt%)	
Carbon	43.33	Moisture	8.16
Hydrogen	5.85	Volatile	70.35
Nitrogen	0.88	Fixed Carbon ^a	10.97
Oxygen ^a	49.16	Ash	10.52
Sulphur	0.79		

^aCalculated by difference.

3.2 Kinetic parameters

The kinetic parameters of horse manure during pyrolysis is investigated using TGA. The mass loss during thermal decomposition of horse manure in an inert environment under four different heating rates of 1, 2, 5 and 10 °C/min is shown in the graph of TG (Figure 1a) and graph of DTG as a function of temperature (Figure 1b). The mass loss curve of dried horse manure has two distinct mass loss regions, mainly the dehydration region (30-110 °C) and the devolatilization region (190-900 °C). The devolatilization region consists of the decomposition of hemicellulose and cellulose (190-400 °C) and lignin (190-900 °C), which has also been reported by Yang et al. (2004). Rapid weight loss begins at about 190 °C and slows down when approaching 400 °C before decreasing to final temperature. The remnants from the devolatilization process is about 18% of the initial amount which is comparable with the total amount of fixed carbon and ash content obtained through proximate analysis of dried horse manure.

From the effect of heating rate as shown in Figure 1a and 1b, higher heating rate causes a shift of TG and DTG graph towards the right which indicates higher temperature is needed to initiate devolatilization of the samples for higher heating rate. Figure 1 shows that at 1 °C/min, rapid mass loss starts at about 180 °C while at 10 °C/min is about 220 °C. For the case of DTG curve in Figure 1b, the maximum temperature peak is shifted towards the higher temperature zone. The maximum temperature peak for 1 °C/min is 290.21 °C while for 10

$^{\circ}\text{C}/\text{min}$ is 329.6°C . This effect is due to thermal lag within the sample, or also known as the phenomenon of heat transfer limitation. As higher heating rate is imposed on the sample, the expected devolatilization of sample is forced to be completed within a shorter time frame, hence higher temperature during decomposition is needed. Besides, this also explains the higher DTG peak value for $10^{\circ}\text{C}/\text{min}$ when compared with $1^{\circ}\text{C}/\text{min}$ as higher heating rate causes faster reaction. Similar curve behavior has been reported by Huang et al. (2016) when pyrolysing soybean straw in inert environment. Slopiecka et al. (2012) stated that the DTG curve is be the same for an identical heating rate. They showed that when pyrolysing poplar and beech wood samples both at $5^{\circ}\text{C}/\text{min}$, the curves did not shift.

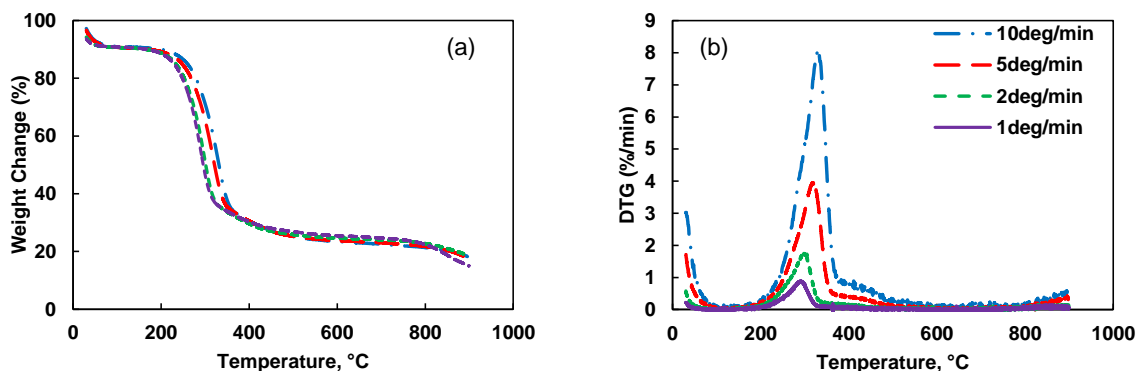


Figure 1: A plot of TGA (a) and DTG (b) of horse manure at heating rate 1, 2, 5 and 10 $^{\circ}\text{C}/\text{min}$

In this study the conversion range of 0.15-0.7 is used for kinetic evaluation as shown in Table 3. In literature, conversion range of 0.3 and 0.7 is selected for kinetic analysis to avoid inaccuracy due to DTG peak tails (Abd-Elghany et al., 2017) but in this study, evaluation of kinetics is done at an earlier conversional fraction due to its alignment with conversion temperature range and low moisture content. Linear regression graphs shown in Figure 2 have high correlation factor and is used to determine the activation energy.

From the activation energies calculated at various conversional fractions using FWO and KAS methods, it is clear that the activation energy is a function of conversional level. The changes of E_{α} at different conversion fraction indicates the existence of complex reaction during devolatilization which involves multi-step mechanism that takes place within the solid sample (Islam et al., 2015). The range of activation energy obtained using FWO is 176.17-293.57 kJ/mol while by KAS is 175.63-300.14 kJ/mol. The changes in E_{α} shown in Table 3 shows the inconsistency of reaction mechanism throughout the whole devolatilization period and is dependent on α . Kissinger method calculates E by linear regression and peak degradation temperature from DTG graph. The values of E_{α} and A obtained shown in Table 4 are averaged throughout the entire pyrolysis process, which are 148.47 kJ/mol and $3.59 \times 10^{12} \text{ s}^{-1}$. Iso-conversional model-free methods (FWO and KAS) derives the E_{α} without considering the type of reaction model while maintaining reliable multi-step kinetics. This is slightly different with Kissinger method which gives an average E_{α} value and the detail kinetic mechanism is not revealed.

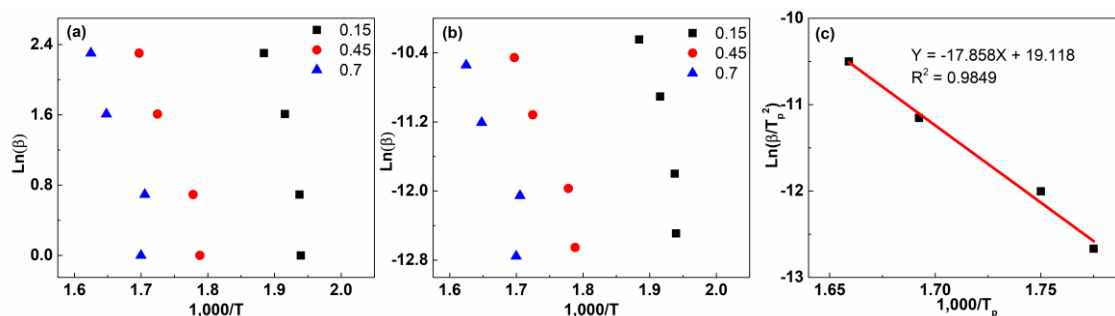


Figure 2: Linear plot of (a) FWO, (b) KAS and (c) Kissinger methods

Higher heating rate enhances the interaction among molecules while lower heating rate reduces the elemental interaction. Hence, TGA analysis with lower heating rate gives result that is more reliable and clearer in the compositional degradation region (Cao et al., 2014). In this study, the TG data obtained at the lowest heating

rate (1 °C/min) will be used to evaluate the thermodynamic parameters of horse manure. The thermodynamic parameters in Table 3 elucidates the reactions of horse manure decomposition during pyrolysis. The pre-exponential values obtained through FWO and KAS methods are of the order of 10^{15} to 10^{26} while the values obtained through Kissinger method is of the magnitude 10^{12} . The vast range of pre-exponential value indicates the complicated chemical reaction during reaction due to the complex structure of horse manure. There is an exceptionally high pre-exponential value (10^{26}) at conversion fraction of 0.15 followed by a drop in value (10^{20}) at $\alpha = 0.2$. This is probably due to the extra energy needed during initiation of hemicellulose and cellulose degradation. When the energy barrier is overcome, the continuation of horse manure degradation is carried out at lower energy level. Towards the conversional fraction of 0.7, pre-exponential value rises owing to the degradation of remaining lignin components. Higher pre-exponential value indicates the requirement of higher molecular collision which requires more heat to be transferred and is adjacent to the activation energy needed as shown in Table 3.

Table 3: Kinetics and thermodynamics parameters value calculated by FOW and KAS methods

α	FWO					KAS				
	E (kJ/mol)	A (s^{-1})	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol)	E (kJ/mol)	A (s^{-1})	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol)
0.15	293.57	1.8×10^{26}	289.28	151.24	245.03	300.14	7.7×10^{26}	295.85	151.14	256.87
0.20	227.19	1.0×10^{20}	222.81	152.44	124.91	230.07	1.9×10^{20}	225.69	152.38	130.13
0.25	210.10	2.4×10^{18}	205.65	152.81	93.80	211.93	3.6×10^{18}	207.48	152.77	97.12
0.30	200.68	3.1×10^{17}	196.17	153.02	76.59	201.89	4.0×10^{17}	197.37	152.99	78.78
0.35	192.26	4.9×10^{16}	187.69	153.22	61.19	192.91	5.6×10^{16}	188.34	153.21	62.37
0.40	185.61	1.1×10^{16}	181.00	153.39	49.02	185.81	1.2×10^{16}	181.20	153.38	49.38
0.45	180.78	4.0×10^{15}	176.13	153.51	40.16	180.65	3.9×10^{15}	176.00	153.51	39.91
0.50	177.46	1.9×10^{15}	172.78	153.60	34.04	177.07	1.8×10^{15}	172.38	153.61	33.33
0.55	176.17	1.4×10^{15}	171.44	153.63	31.61	175.63	1.3×10^{15}	170.91	153.65	30.64
0.60	176.78	1.6×10^{15}	172.01	153.62	32.65	176.18	1.4×10^{15}	171.42	153.63	31.57
0.65	180.21	3.5×10^{15}	175.40	153.52	38.83	179.72	3.1×10^{15}	174.90	153.54	37.92
0.70	190.21	3.1×10^{16}	185.32	153.27	56.89	190.12	3.1×10^{16}	185.23	153.27	56.73

Table 4: Kinetics and thermodynamics parameters value calculated by Kissinger method

Equation	E (kJ/mol)	A (s^{-1})	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol)
$y = -17.858x + 19.118$	148.47	3.29×10^{12}	143.86	154.43	-18.77

Enthalpy change, ΔH is the difference in energy level between reagent and activated complex. The overall positive enthalpy change affirms that pyrolysis of horse manure is an endothermic reaction where heat energy is readily absorbed by the system for breaking and formation of new chemical bonds. The difference in free Gibbs energy, ΔG is the total increase in energy of a system during the approach of reagents and the formation of the activated complex. Overall the ΔG increases steadily by a small amount as the conversion of horse manure continues. Endergonic reaction occurs throughout the process where this occurrence is non-spontaneous. As pyrolysis continues, more energy is required by the horse manure to undergo conversion. Entropy change, ΔS , is the measure of degree of disorder of a system where it explains the closeness of a system to its own thermodynamic equilibrium. As shown in Table 3, ΔS is high at initial conversional fraction but decreases as conversion of sample increases. This indicates that as horse manure is being degraded thermally, more reagent are being converted causing the unreacted reagent to decrease. However, towards the conversional fraction of 0.7, higher temperature ($T \sim 590$ °C) caused the formation of char from lignin, hence a spike in ΔS value is observed. The ΔS obtained for FWO and KAS methods at conversion fraction of 0.7 (-56 J/mol) is higher compared to Kissinger method (-18.77 J/mol). This is because at 70% of conversion, only partial char is being formed and volatiles are still present within the sample. The reactivity of the sample is still high but Kissinger method evaluates the sample at complete conversion. As the reaction approaching completion, most of the manure has been converted into char and the negative entropy value indicates the formation of activated complex which is more organized compared to the initial substance (Xu and Chen, 2013).

4. Conclusions

Kinetics of horse manure during non-isothermal pyrolysis was evaluated experimentally by using Model-Free methods. The FWO and KAS methods are more accurate as the kinetics parameters were evaluated based on

interval conversional level of horse manure while Kissinger method provides an overall estimation of the parameters based on the completeness of the entire pyrolysis process. The activation energy obtained from FWO method is 176.2-293.6 kJ/mol, while by KAS method is 175.6-300.1 kJ/mol. Higher energy is required for the initiation of devolatilization process to overcome the activation energy barrier. Towards the end of the pyrolysis process, higher energy is also required where the lignin in the horse manure is being degraded into char. The result shows that horse manure is a potential pyrolysis feedstock with high volatile content, and less than 20 % of char and ash are left after pyrolysis. The data can serve as a useful reference for pyrolysis reactor design.

Acknowledgments

Financial support from the Malaysian Ministry of Higher Education and Universiti Teknologi Malaysia (International Incentive Grant - vote no. 01M20) is gratefully acknowledged.

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