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Pyrolysing Horse Manure via Microwave-Induced Heating for Bioenergy Recovery

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Transforming waste to energy is essential in view of the need to search for greener and more sustainable energy sources. Such transformation of energy is also aligned with the aim of reducing excessive waste generation whilst creating potential biofuel pathways for power generation. In the present study, animal waste in the form of horse manure is being used as feedstock to undergo microwave-induced pyrolysis via a fixed-bed pyrolysis rig. The relationship of the pyrolysis parameters such as pyrolysis temperature of 350 and 550 °C, carrier gas flow rate of 0.5 and 1.5 L/min and ratio of horse manure to activated carbon blend of 1:2 and 1:1, with the yield of pyrolysed products is studied. The derived pyrolysis products in the form of solid, liquid and gaseous are characterised and quantified. Result shows that the highest yield of solid, liquid and gaseous products obtained are 78.8 wt%, 24.7 wt% and 34.2 wt%. Solid yield is observed to decrease with increasing pyrolysis temperature while gaseous yield shows a reverse trend. Higher carrier gas flow rate is observed to lower the generation of gaseous and liquid yield while increasing the solid yield. Higher amount of activated carbon within the feedstock is seen to lower the solid yield but increase the gaseous and liquid yields. The liquid yield is found to contain 55.78 wt% of phenolic compounds while gaseous product consists of up to 55 vol% of syngas. The control of the operating conditions in pyrolysis rig enables the production of pyrolysis end products in different phases, generating useful bioenergy and biofertilizer products in the context of circular economy.

1. Introduction

A joint study by the U.S Department of Energy and Agriculture in 2005 shows an approximate 35 M dry t of dry animal manure is produced from the agricultural land. From an energy point of view, these manures consist of 0.43×10^{18} J worth of equivalent energy, which amounts to 15 % of the total biomass energy consumed annually in the U.S (Perlack et al., 2005). The land and water pollution from illegal dumping or unsystematic disposal of animal waste have also raised concerns among the public. Effective methods to process these animal waste for safe disposal or upgrade them into higher value end products are in demand. Thermochemical conversion technologies present a viable solution that could achieve both the needs of waste disposal and waste utilisation. Thermochemical conversion refers to a process where a sample is heated to elevated temperature in an oxidative or inert environment to produce end products in the forms of solid (biochar), liquid (bio-oil) or gas (biogas). In general, such thermochemical conversion technologies are effective due to short processing time, capable of killing pathogens and producing minimal amount of nonbiodegradable sludge (Ro et al., 2010). One of the promising thermochemical conversional processes is pyrolysis which could be applied to animal manure. Various types of animal manure, such as swine manure (Ro et al., 2009), poultry manure (Isemin et al., 2019) and cattle manure (Yuan et al., 2017) have been

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pyrolised for valorization purposes. The generated end products are known to be dependent on the process parameters, such as temperature, catalyst, particle size and gas flow.
Microwave pyrolysis technology has gained much attention due to its capability in heating feedstocks uniformly through convection and conduction (Dong et al., 2018). The use of microwave heating has been reported to produce higher grade bio-oil and syngas concurrently (Hong et al., 2017). However, there is limited work related to the application of microwave-induced pyrolysis on animal waste. Horse manure is a potential biowaste that can be processed for bioenergy recovery. Previous work has shown the kinetics of horse manure during non-isothermal pyrolysis determined via isoconversional methods (Mong et al., 2019). The current study aims to determine the pyrolysis product yield of thermally decomposed horse manure via microwave-assisted heating method. The effects of pyrolysis parameters, such as temperature, catalyst ratio and gas flow on the end-product yield distribution are identified while the pyrolised gaseous and liquid products are characterised.

2. Material and methods

2.1 Material

In this study, horse manure was collected from a horse stable in Universiti Teknologi Malaysia, Skudai, Johor. The horse manure was dried using an electric oven at 120 °C for 24 h for moisture removal. The dried manure was then ground and sieved to the size between 100 and 500 μm, which was then stored in an air-tight container. Coconut shell-based activated carbon, supplied by Concept Ecotech Sdn Bhd, underwent the same heating and processing methods for moisture removal and storage. Horse manure is made up of a majority of lignin content (56 wt%), hemicellulose (23.8 wt%) and extractive (13.9 wt%). It has a majority of volatile composition (70.4 wt%) and a carbon percentage of 43.3 wt% (Chong et al., 2019). The properties of activated carbon used in the present study has been reported (Ng et al., 2017).The pyrolysis feedstock was prepared by blending the ground horse manure with activated carbon at a specific mass ratio using a mixer.

2.2 Experiment apparatus

Microwave-induced pyrolysis of horse manure was performed through a single-mode, domestic microwave oven operated at the frequency of 2.45 GHz with a microwave output power of 1 kW. The schematic diagram of the fixed-bed, batch-typed microwave pyrolysis system is shown in Figure 1. The reactor is made from quartz glass with an internal diameter of 100 mm and height of 250 mm, while the 3-neck lid is made from borosilicate glass with a standard opening of 24/29. A thermocouple that extends to the bottom of the quartz reactor was inserted from the lid to provide instantaneous temperature readings of the feedstock throughout the entire experiment. Besides, a thermocouple is also used as a feedback mechanism to the PID temperature controller to keep the temperature of the reacting feedstock at a specified range. Temperature data was recorded using the Pico Logger software at 10 s interval. Two Graham coil condensers, each with an effective length of 300 mm, were positioned in series for vapor condensation. A circulating water chiller was used to keep the condenser chilled at 9 °C. Nitrogen gas (purity of 99.99 %) was used to purge the system to ensure an inert environment for pyrolysis.

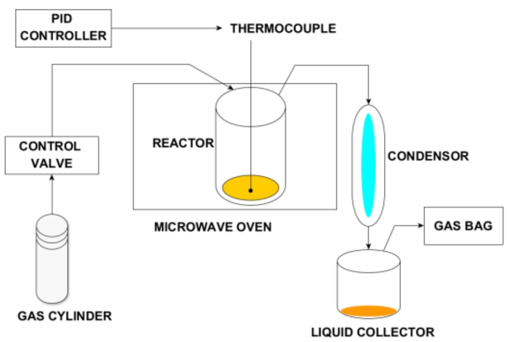

Figure 1: Schematic diagram of the fixed-bed, microwave pyrolysis rig

2.3 Experimental

The blended feedstock, comprising horse manure and activated carbon, was transferred into the quartz reactor and then placed within the microwave cavity. The weight of feedstock for each run was fixed at 60 g and filled to the depth of 20 mm in the quartz reactor. Three pyrolysis parameters, namely temperature (350 and 550 °C), carrier gas flow rate (0.5 and 1.5 L/min) and horse manure to activated carbon ratio, HM:AC (2:1 and 1:1), were investigated. The position of quartz reactor was placed in the pathway of microwave propagation in order to obtain maximum exposure. After 15 min of nitrogen purging at 0.5 L/min, the power supply was turned on. While allowing the carrier gas to flow continuously, the feedstock was then exposed to microwave radiation for 40 min, followed by cooling of 20 min. The vapor evolved during the pyrolysis process was directed to two serially connected condensing channels, which were kept at 9 °C. Condensable and non-condensable gases were referred to as the liquid and gas yield. The condensed liquid was collected from the flask positioned directly below the condenser, while the gaseous product was passed through a silica bed. The gas sample was collected at every 5 min interval for 8 s using a 1 L Tedlar gas sampling bag. The solid remained within the quartz reactor was harvested mechanically, weighed and stored in a test tube.

2.4 Quantification methods

There are five types of end products that can be collected from the microwave-induced pyrolysis experiment, namely solid, liquid, gas, water and sediments. The solid yield was obtained directly by weighing the mechanically harvested leftovers within the quartz reactor. The liquid yield was obtained by weighing the flask at the end of the condensing channel. Water content and sediments were obtained by weighing the experimental apparatus. The increase in the silica gel weight indicates the entrapment of water vapor and ash within the gaseous products. By heating the silica gel at 105 °C for 3 h, the loss in weight indicates the amount of water present within the silica gel. Sediment content is the remaining gain in weight for the silica gel when comparing the silica gel weight before and after the pyrolysis process. The same method was also applied to measure the weight of the sediments trapped in the condenser and connecting tube with the quartz reactor. The gas yield is quantified by mass balance equation by considering all the product yield using Eq(1), where

$$Gas\ yield\ (\%) = \frac{100 - solid - liquid - water - ash}{Horse\ manure\ feedstock} \times 100\% \quad (1)$$

The compounds in the liquid product were analysed using gas chromatograph (Agilent HP 6890) coupled with a mass spectroscopy. A capillary column (Agilent 19091S-433 HP-5MS) was used and operated in a continuous flow mode, with an inlet pressure of 8.12 psi and 20:1 spilt ratio. Liquid compounds detected were compared with the NIST08 mass spectral library. Gas composition was analysed using a gas chromatography (Agilent HP 6890) coupled with a thermal conductivity detector. The oven temperature was set to 60 °C for 1 min, then was raised to 190 °C at a rate of 15 °Cmin^{-1}. For each run, 2 mL of bio-gas was injected into the column and the data was recorded at 50 Hz. The gas calorific value was calculated using Eq(2).

$$LHV\left(\frac{MJ}{Nm^3}\right) = \frac{[H_2 \times 107.98 + CO \times 126.36 + CH_4 \times 358.18 + C_2H_2 \times 56]}{1000} \quad (2)$$

3. Result and discussion

3.1 Temperature profiles

The domestic microwave oven was calibrated prior to the experiment. The actual microwave output power is about 60 % of the rated microwave power output, indicating a power efficiency of 60 %. Figure 2 shows the temperature profile of horse manure during microwave radiation where the highest temperature achievable by dried horse manure was about 200 °C.

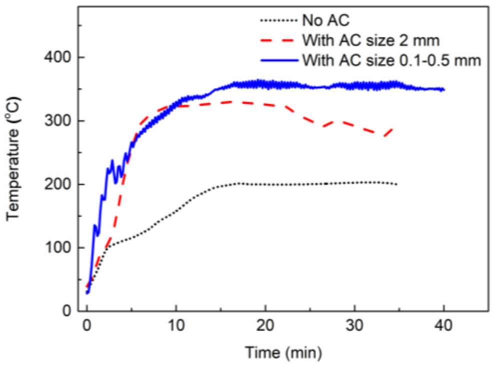

Figure 2: Temperature profile of feedstock within microwave cavity with and without microwave receptors

To elevate the pyrolysis temperature, coconut-based activated carbon was used as microwave receptor blended with dried horse manure to enhance the absorption of microwave energy. The activated carbon with the size about ~2 mm was effective in improving heat absorption, as shown in Figure 2, but the temperature fluctuation indicates the issue of uneven heating. When using ground activated carbon with the size similar to those of dried horse manure (100 – 500 µm), a consistent heating temperature was achieved, signifying the uniformity of heating achieved by the blends. The use of finely ground granular activated carbons allows high contact area with the feedstock, permitting conduction of heat to effectively take place during pyrolysis. The pyrolysis temperature of 350 °C achieved was rather constant for reaction to take place. Another factor that contributes to the temperature fluctuation is the power cut by the magnetron during heating as part of the safeguard to the equipment, which causes interval heating and cooling effect. This phenomenon was also reported in other microwave-induced pyrolysis experiments (Wan Mahari et al., 2018).

3.2 Product yield

Under the selected range of experimental parameters, the solid, liquid and gaseous yields obtained from the microwave-induced pyrolysis of horse manure were in the range of 30.9 – 78.8 wt%, 11.1–24.7 wt% and 7.1–34.2 wt%. The lowest solid yield was 30.87 wt% as shown in Table 1, which corresponds to the high volatile content (~70 wt%) of horse manure (Chong et al., 2019) where most of the volatile substance had been valorised during decomposition. The high solid yield may be due to incomplete decomposition. As for the minor end products, sediments and water yields were recorded to be in the range of 0.5–3.8 wt% and 1.2–6.5 wt%. Water yield was found to be low as the horse manure had been pre-dried prior to experiment. The presence of water content from the pyrolysis process could be due to the moisture trapped within the cellulosic components in the horse manure, which was released during the thermal decomposition process. As for the sediments, the ash created during the pyrolysis process may be carried downstream via the carrier gas, depositing on the wall of the glassware as well as on the silica gel. The sediments were observed to comprise of ash content within the feedstock, either unreacted, partial or fully reacted horse manure.

Table 1: End product phase distribution and yield for microwave pyrolysis of horse manure

Temperature (°C)	Ratio (HM:AC)	Gas flow (L/min)	Solid (wt%)	Liquid (wt%)	Gas (wt%)	Sediment (wt%)	Water (wt%)
341	2:1	0.5	54.5	16.8	22.5	2.8	3.5
530	2:1	0.5	58.7	15.7	20.5	2.0	3.1
354	1:1	0.5	57.0	17.5	20.4	1.4	3.7
533	1:1	0.5	30.9	24.7	34.2	3.7	6.5
360	1:1	1.5	68.0	13.3	14.4	3.1	1.2
517	1:1	1.5	49.0	18.4	25.1	3.8	3.6
350	2:1	1.5	77.0	12.6	7.2	0.8	2.6
618	2:1	1.5	78.8	11.1	7.1	0.5	2.5

The influence of pyrolysis temperature, carrier gas flow rate and ratio of horse manure to activated carbon ratio (HM:AC) on the distribution of products from microwave-induced pyrolysis of horse manure was further studied. Figure 3 shows the yield distribution of products from horse manure at different pyrolysis parameters. On the effect of HM:AC ratio, it was observed that at higher proportion of activated carbon, solid yield was observed to reduce while liquid and gas yields increased. The use of higher amount of activated carbon allowed more microwave energy to be absorbed and converted into heat. The heat generated was then dissipated effectively to the feedstock via conduction. The presence of activated carbon also acts as a layer of insulation that reduces heat loss (Idris et al., 2018). Improved heat transfer facilitates pyrolysis reaction to occur, thus it is expected that more pyrolysed compounds can be attained. The heat is essential in breaking down the large molecular compounds into small volatile molecules, which are then removed by the carrier gas that eventually formed the condensable (liquid) and non-condensable (gas) vapour. Temperature effect on product phase distribution is similar to the effect of HM:AC ratio, where elevated temperature increases the liquid and gas yield while lowering the solid yield. This is due to both process parameters improve the heat transfer process and enable the absorption of more heat by the feedstock. At the carrier gas flow rates of 0.5 and 1.5 L/min, the increase of pyrolysis temperature resulted in significant increase of gaseous yield for HM:AC ratio of 1:1. More energy was supplied to the pyrolysis sample at higher heating temperature, thus enabling higher rate of reaction. The large molecules from the manure was decomposed into smaller molecules light enough to be carried away by the inert gas. For HM:AC ratio of 2:1, the effect of temperature was not evident as the heat provided was not sufficient to valorise the feedstock into smaller molecule compounds.

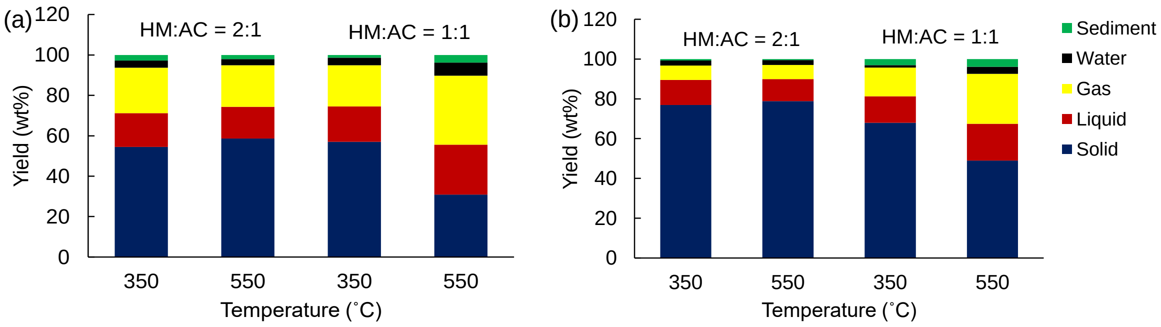

Figure 3: Yield distribution of horse manure microwave pyrolysis at flow rate of (a) 0.5 L/min and (b) 1.5 L/min

The effect of carrier gas flow rate on the distribution of end products can also be observed by comparing Fig. 3a and 3b. Solid yield was found to increase with carrier gas flow rate while liquid and gaseous product yields decreased. This phenomenon is likely due to the directional flow of the carrier gas. The carrier gas flowed into the reactor from the left-neck on the top lid (downwards) then exited from the right-neck on the same lid (upwards). During pyrolysis, as the horse manure is being decomposed, volatile will be evolved from within the feedstock, which will then be swept away by the gas flow moving out of the reactor. When the flow rate increases, the carrier gas enters the reactor chamber at a higher rate. The force of carrier gas entering the reactor might be larger than the force of volatile emerging from within the feedstock. This causes a portion of the volatile evolved being pushed back into the feedstock, clogging the pores and pathway available for others volatile to be released. This would then lead to the observed higher solid yield and lower liquid and gaseous yield, where Hornung (2013) also explained the varying reactor design will affect the end-product yield distribution. Such trend relating higher gas flow rate with lower solid yield has also been reported by Valliyappan et al. (2008) in the microwave pyrolysis of crude glycerol, where the carrier gas entering the reactor from above and leaving the reactor via an opening at the bottom of the reactor. A one directional flow of gas into and out of the reactor could result in a very different yield distribution behaviour.

3.3 Characterization of products

The highest yield of gas and liquid products obtained from the pyrolysis test was characterised to identify the constituent components. From Table 1, it is observed that the case with set temperature of 550 °C, HM:AC ratio of 1:1 and 0.5 L/min of flow rate gave the highest yield of liquid and gas products. Table 2 shows the gaseous product composition contains 35.4 vol% of H_2 and 20.7 vol% of CO, making up a total of 55 vol% of combustible synthesis gas (H_2+CO). In comparison with the current study, pyrolysis of swine and chicken manure at 620 °C was reported to have lower syngas proportion of 25.6 wt% (Ro et al., 2010). The lower heating value of the gaseous product is 6.32 MJ/Nm^3. For the liquid composition shown in Table 3, phenols (55.78 wt%) made up most of the liquid yield, followed by ketones (23.91 wt%). Phenols can be extracted from bio-liquid and used for the production of phenolic resin, which is a type of polymer with good mechanical, heat and impact resistance (Dixit et al., 2016).

Table 2: Gas products obtained at T=550 °C, HM:AC=1:1, N_2 flow rate=1 L/min

H_2 (vol%)	CO_2 (vol%)	O_2 (vol%)	CO (vol%)	LHV (MJ/Nm^3)	Ratio (H_2/CO)
35.35	13.91	30.06	20.67	6.32	1.71

Table 3: Liquid compounds obtained at T=550 °C, HM:AC=1:1, N_2 flow rate=1 L/min

Pyridine (wt%)	Furan (wt%)	Phenols (wt%)	Ketones (wt%)
14.26	6.05	55.78	23.91

4. Conclusion

Microwave-induced pyrolysis of horse manure blended with activated carbon is found to be a reliable method for valorization of animal waste to produce bioenergy. Horse manure has been successfully converted into three main end products in solid, liquid and gaseous form via the microwave-assisted thermal decomposition method. The pyrolysis temperature, HM:AC ratio and carrier gas flow rate are important parameters that affect the product yield distribution. The increase of pyrolysis temperature and HM:AC ratio reduced solid yield and increased liquid and gas yields. The parametric study shows the highest yield obtained for solid, liquid and gaseous products are 78.83 wt%, 24.7 wt% and 34.17 wt%. The relatively high concentration of syngas can be used as fuels, while the bioliquid produced contains valuable compounds such as phenolics, ketones, pyridine and furan.

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