ASME Journal of Energy Resources Technology
Online journal at:
https://asmedigitalcollection.asme.org/energyresources

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Experimental and Mathematical Investigation of Thermochemical Conversion for Horse Manure

Horse manure is one of the highest potential biowastes for heat and power generation. This article investigates the experimental and mathematical modeling of thermochemical conversion for horse manure. As one type of thermochemical conversions, the pyrolysis process was carried out at eight different heating rates on horse manure using three parameters: the extent of reaction, the rate change of the extent of reaction, and differential thermal analysis (DTA), all used to determine kinetic data that will be validated with a mathematical model. Slow pyrolysis: below 15 °C/min showed optimistic results of obtaining exothermic reaction over a wide range of temperature which makes it self-sustainable with steady heat generation. Also, low heating rates allowed a quasi-equilibrium state through slow heating with a minimum delay in response for any transient error that could be generated from differential thermal gravimetry (DTG) device. [DOI: 10.1115/1.4065956]

Keywords: biomass, horse manure, pyrolysis, thermochemical, biomass modeling, renewable energy, alternative energy sources, energy systems analysis, fuel combustion, heat energy generation/storage/transfer, power (co-)generation

Introduction

The modern world today relies overwhelmingly on energy, powering everything from lights to communication devices. As the population increases and more technology is developed, more energy is needed to meet the demand. From the beginning of human existence, the demand for energy has greatly increased, leading to total dependence on fossil fuels such as oil, coal, and natural gas. Only in the last few decades has renewable energy fulfilled a small quantity of this global energy demand. In 2021, according to the Energy Information Administration, the US primary energy consumption was around 98 quadrillion British thermal unit (Btu) (over 100 quintillion joules), which made up 16% of the world's primary energy consumption (equivalent to approximately 604 quadrillion Btu or over 637 quintillion joules). Seventy-nine percent of the US energy consumption was from fossil fuels and only 12% was from renewable energy, while the rest was from nuclear reactors [1]. This massive energy reliance on fossil fuels is alarming for many reasons: The finite amount available of these resources, the rapid increase in energy demand, and the high amount of pollution caused by the harmful gases, namely CO_2, which are emitted when burned.

In response to these global issues, there has been a movement to shift toward renewable energy sources such as geothermal, solar, hydro, wind, and biomass. These energy sources have disadvantages, such as air pollution and land usage; for example, implementing solar panels and wind farms requires the use of a huge land surface. In addition, there are negative effects on wildlife, such as birds that are killed by the blades of the wind turbines and fish that are killed by the blades of hydro turbines. However, the limitations in energy and damage from energy obtained from renewable resources are drastically lower than the energy derived from fossil sources. In the United States, wind energy is the largest renewable energy resource, providing 27%; both hydroelectricity and biofuel come second with 19% each; wood with 17%; solar with 12%; and finally, biomass from waste and geothermal respectively with percentages of 4% and 2% [2].

Biomass energy resources are organic materials derived from living organisms that can be used as renewable sources of energy. Some of the most common types of these organic organisms come from agricultural crops, forestry crops, municipal waste, sewage, and animal manure. Agricultural crops and residue including residue from corn, sugarcane, corn stalks, and wheat straw residues. These sources, which produce ethanol fuel, are a decent

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Contributed by the Advanced Energy Systems Division of ASME for publication in the Journal of Energy Resources Technology. Manuscript received May 26, 2024; final manuscript received July 9, 2024; published online August 20, 2024. Assoc. Editor: Ashwani K. Gupta.

substitute for gasoline [3]. Forestry crops and residues are sources of energy production that can be obtained from residual leftovers from trees or from plantings specifically for biomass use. The methods for biomass production use short rotation coppicing, which involves the dense cultivation of high-yield willow species. These plants are harvested within an average cycle of 3 years [4]. A second method uses short rotation forestry, which involves the planting of trees and subsequent harvesting once the trees have grown to a size of roughly 10–20 cm in diameter at chest height. This growth process typically takes between 8 and 20 years. Finally, the third method comes from creating wood pellets, small pieces of compressed wood, such as biofuels. Municipal solid waste (MSW), disposed items such as garbage or trash, consists of a variety of materials generated by households, businesses, and institutions. According to the Environmental Protection Agency (EPA), MSW does not include waste from construction and demolition debris, municipal wastewater treatment sludge, and nonhazardous industrial waste. According to the EPA, the total MSW generated material in 2018 in the United States was 292.4 million tons [5]. Sewage is discharged wastewater from households and industrial and institutional facilities through sewage systems. In the United States, 34 billion gallons of wastewater is processed daily by more than 16,000 wastewater treatment facilities [6]. One method of converting sewage into energy is through a process known as anaerobic digestion, where biogas is produced by the process of bacteria, which breaks down the organic material in the absence of oxygen. Another method is known as sludge incineration, where sewage is dried and directly used as a fuel source. Animal manure is a byproduct of livestock farming. Commonly, this organic material is used in agriculture to fertilize and condition the soil but is also used as a source of energy [7]. The distinctive characteristic of animal manure is that due to its wide availability that permits it to not only be a powerplant product, but it can also be implemented on a residential scale. In other words, the abundant availability of animal manure positions it as a significant feedstock for power plants, enabling large-scale energy production. Additionally, on a residential scale, this manure can be processed for various applications for example conversion to pellets to be used for cooking or heating. According to the United States Department of Agriculture's 2017 Census, the United States had about 94.8 million cattle and calves, 74.6 million hogs and pigs, and over 3876 million chickens [8]. The amount of waste produced can be estimated by using the single animal generation amount and multiplying it by the total animal population. A mature dairy cow can produce around 14 gallons (120 pounds) of feces and urine, where at least 12% is solid [9]. A 1250-pound beef cow generates 45 pounds of manure daily, while pigs generate an average of 11 pounds and an adult horse produces about 37 kg of manure daily [10]. It is also worth noting that horse manure in its natural form is 75% dry while cow manure is only 10% dry [11], which gives the former the advantages in terms of drying, storing, and transporting. It has been reported that certain countries such as Argentina, China, Brazil, and Canada consume up to 100,000 horses for meat annually [12]. The commercial breeding of horses produces substantial amounts of manure that need to be disposed of. Although part of the manure can be recycled as fertilizer for soil enrichment, excess manure can be difficult to dispose of [13]. Consequently, the utilization of animal manure as another source of energy comes into play.

Converting biomass into energy can be done through several processes, each process is suitable for specific application based on the type of biomass feedstock, the desired form of energy output, and various economic and environmental factors.

Biochemical conversion uses biological organisms such as bacteria and enzymes to break down biomass to produce clean energy [14]. This process can be carried out in various ways, such as anaerobic digestion, where microorganisms break down biomass in an oxygen-free environment to produce biogas (mainly composed of methane and carbon dioxide) and a nutrient-rich digestate [15]. Previous literature indicates that anaerobic digestion effectively converts raw solids and organic waste into energy in biogas or other forms. Also, one of the advantages of the process is the low capital cost [16]. In Stuart's 2006 [17], several process advantages are listed, such as the wide availability of resources, the economic benefit, and the flexibility in scaling up the technology. On the other hand, many disadvantages, such as environmental concerns and fluctuation in load, are also discussed. Fermentation is when sugar in biomass is converted into alcohol, like ethanol, using yeast or bacteria. Corn and sugarcane are the most used biomass feedstocks [18]. Transesterification is where biomass feedstock like vegetable oils, animal fats, or waste cooking oils undergo a chemical reaction, called transesterification, with alcohol to produce biodiesel and glycerol [19].

Thermochemical conversion is the conversion of biomass into useful energy that uses high temperatures and chemical reactions in the presence or absence of oxygen. Methods in this process are direct combustion, pyrolysis, and gasification [20]. Direct combustion is the process of burning biomass to produce heat to generate electricity. Direct combustion could produce energy for heating purposes or for generating electricity, creating steam that rotates a turbine to convert the kinetic energy into electrical energy by using a generator. Da Lio et al. investigated the efficiency of utilizing the combustion process on horse manure as an energy source. The challenge in this process is the heterogeneous nature of horse manure and the wet mixture of bedding materials and feces, which require a particular furnace design to function. Also, another issue is the significant presence of nitrogen in the fuel, which often leads to ammonia emission, which is hazardous.

A similar study was done in 2009 by Lundgren and Petterson who found that the emission of carbon monoxide (CO) was between 30 and 150 mg/Nm^3 and the NO_x was between 280 and 350 mg/Nm^3. Suggested solutions in the study wadded other types of biomasses, such as wood shavings and sawdust, to improve the process.

Also, lower emission of CO is achieved if the water content is kept below 50 wt% even though the process of combustion using horse manure is still feasible; however, drying the sample is still a crucial issue [21,22].

Gasification: even though combustion is the simplest and most straightforward method of converting biomass into energy thermochemically, it has a lower efficiency in heat generation. Besides, gasification is more efficient and has many more advantages over combustion. Gasification requires less feedstock and converts feedstock into multiple types of energy that could be used for heating, transportation, or power. Gasification has a significantly lower emission of greenhouse gases such as nitrogen and sulfur [23]. In gasification, biomass is partially oxidized by supplying oxygen, air, or steam to the reaction as a gas agent. Biomass is heated, and the reaction produces syngas, such as hydrocarbons [24]. This syngas can be used as fuel for power generation or further processed to produce biofuels or chemicals. Gasification can convert the burden of the animal manure into fuel participating in fostering energy security and achieving energy sustainability [25,26]. Amano et al. [27] conducted a study to utilize carbon dioxide as a gas agent in gasification to decrease the amount of greenhouse gases emitted. An experimental investigation was conducted on chicken manure using carbon dioxide as a gas agent to study the effect of the particle size on the residual mass and conversion rate. The results show that larger particles are correlated to lower conversion rates and higher residuals [27]. Amano et al. investigated the evolutionary behavior of syngas composition using pyrolysis with nitrogen being the agent gas and gasification at different temperatures and different oxygen concentrations. The different temperatures used were 600–1000 °C with an increment of 100 °C. The oxygen concentrations in nitrogen used were 21% and 10%. The gas evolved was quantified using gas chromatography. Amano et al. concluded that higher oxygen concentration (21%) generated higher energy yields versus lower concentration (10%) [28]. In addition, Kumar et al. [15] state that one of the advantages of biomass gasification is that it occurs at lower temperatures than coal gasification because biomass is more reactive. Therefore, greenhouse gas emission is decreased because lower temperatures diminish the extent of heat loss as well as reduce material defects associated with higher temperatures [15]. Trninic et al. [29] in their paper "Biomass Gasification Technology: The State-of-the-Art Overview" conducted an overview of biomass gasification technologies and evaluated their advantages and disadvantages. It was stated that the temperature was the most important parameter to control the operation of the gasification process. Higher temperatures lead to higher gas yield due to the higher conversion efficiency. Besides temperature, other aspects had an impact on the efficiency of the gasification process: the agent gas (oxygen, steam, or air), the equivalence ratio (excess air ratio), pressure, residence time, and the shape and size of the sample. It was concluded that even though gasification was among the most restrictive processes for converting biomass to energy, it still had many challenges, such as the preheating requirements before the process and the high cost of cleaning the device to prevent contamination [29].

Pyrolysis is a thermochemical process of heating biomass in the absence of oxygen, which leads to the decomposition of biomass into solid, liquid, and gaseous products. This process breaks down the complex organic compounds into simpler molecules, also referred to as thermal cracking. Pyrolysis can produce biochar, bio-oil (also known as pyrolysis oil), and syngas (a mixture of carbon monoxide and hydrogen), which can be further processed into fuels or chemicals [30]. Selim et al. investigated the process at the same lab in 2021 using chicken and cow manure with different heating rates. This study used pyrolysis for each manure type with eight different heating rates of 5–40 °C/min. The results showed different temperatures of thermal degradation for each manure type. For chicken manure, thermal cracking, which is a chemical process of breaking down large compound hydrocarbon molecules into smaller ones by applying an adequate amount of heat, is associated with hemicellulose decomposition which occurs at 250 °C, while for the cow manure, it occurs at 300 °C. For cellulose decomposition, the thermal cracking temperature occurs at 300 °C and 470 °C for chicken and manure, respectively. The results concluded that pyrolysis with slower heat rates allows for a quasi-equilibrium state [31]. In another report, Selim et al. investigated the effect of different heating rates and the gas agent type in the thermochemical conversion process. The manure type used in this study was chicken, and the gas agents were nitrogen, air, and carbon dioxide. After conducting a thermogravimetric and differential thermal analysis, results showed that the lowest rates were recommended as they provided adequate time for a quasi-equilibrium reaction. In terms of gas agents, air gasification tended to be the most self-sustainable process as it had a larger temperature range for the exothermic reaction. Pyrolysis using nitrogen also showed a significant range of temperature for exothermic reaction. Moreover, gasification using carbon dioxide showed a more complicated thermal degradation profile [32].

The technique utilized in this study to analyze the data is the thermogravimetric analysis (TGA), which measures the weight changes of a sample at a given time and temperature. The device used for this technique was the Simultaneous TG/DTA Differential Thermogravimetrric/Differential Thermal Analysis (DTG)) from Shimadzu DTG-60AH. The difference between the thermochemical processes is summarized in Fig. 1 where the main difference is the agent gases involved in the reaction, the heat range, and the final product.

Figure 2 shows the DTG apparatus, which is used simultaneously to perform the TGA and differential thermal analysis (DTA). The device consists of three main parts: the first part is the electric furnace, which supplies the required heat of the reaction and can be controlled to generate different heating rates and then maintain the reaction at the constant desired temperature. The second part is the measurement system which consists of rods that are each fitted with thermocouples, where both rods are connected to a sensitive balance mechanism. One of the detector rods is used as a reference/control and carries an empty sample cell, while the other rod is used to measure the changes in mass and temperature of the active

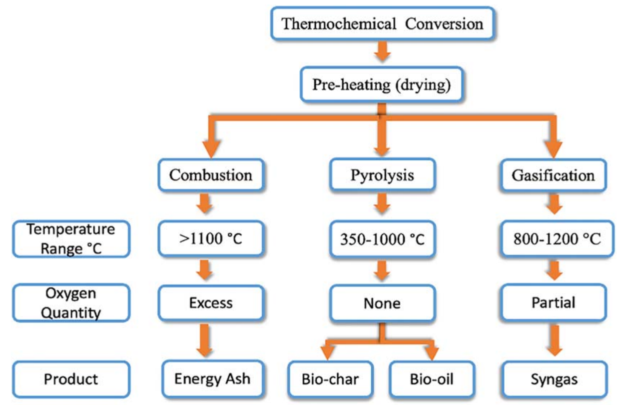

Fig 1 Thermochemical conversion process

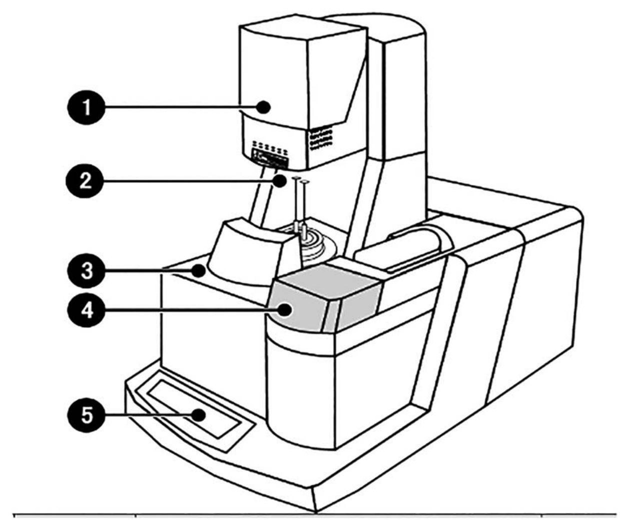

Fig 2 DTG components; 1: furnace cover, 2: detector and reference rods, 3: tray for setting sample pans, 4: autosampler, and 5: kay/display section

sample cell relative to the control cell. The third part of the device is the autosampler, which is a robotic system capable of loading and unloading the samples on the detectors automatically. The weight difference between the two detectors, obtained by the delicate balance, indicates the sample weight. The difference between the voltage readings of the two sensors is measured for the differential thermal analysis. Any dry noncorrosive gas agent can be used with the device. The measurable range of the mass is ±500 mg, with a resolution of 1 μg and ±1% accuracy. The device can provide up to 1500 °C with ±1 °C uncertainty. The thermocouples are Pt-10% pt/Rh thermocouples. The measurable range for the differential thermal analysis is 1000 μV with ±1% µV accuracy and noise level less than 1 μV. To minimize the effect of gas turbulence on the readings, a regular calibration was performed on the device over multiple temperature ranges and operating gas flowrates. Alumina pans were used for all case studies. Equation (1) is used to calculate the extent of reaction, while its rate is calculated by using Eq. (2):

$$\alpha = \frac{w_0 - W_t}{w_0 - w_f} = \frac{\nu_t}{\nu_f} \tag{1}$$

$$\frac{d\alpha}{dt} = \frac{(\alpha_t - \alpha_{t-1})}{\Delta t} \tag{2}$$

Experimentals Procedures. The horse manure composition percentages (cellulose, hemicellulose, lignin, and protein) depend on many factors, such as the horse's age, size, activity, and nutrition.

Forty percent of the horse feedstuff consumption is excreted into manure, and feed with higher fiber content, like hay and grass, which have a lower digestibility [33,34]. This study used a sample from the same horse manure to get microscopic images using a 3D-measuring laser microscope OLS4100 from Olympus. Figure 3, which is a microscopic image of the sample, shows that the sample consists mostly of fibers and undigested hay with a small amount of partially digested feed and some impurities as shown below.

Knowing that horse manure consists mostly of hay, the chemical composition of horse manure can be explained using the chemical composition of hay. A study has been done on a sample from horse feedstock by Danielle Smarsh in an article titled, "Understanding a Hay Analysis." This article reveals the specific quantities of the different nutrients available in hay. The analysis is done in a particular laboratory, and the results are summarized in Table 1 [35].

The sample of hay taken for the analysis is dried completely of its urine and other liquids before the analysis. The water content percentage represents the water in the inner structure of the cells. As seen in the table, the main component of hay is moisture, which makes up about 11–16% of the total mass. A lower percentage of water content, lower than 10%, would lead to the loss of nutrients. Crude protein, which ranges between 8% and 20% of the total weight, is mostly consumed by the horse, where the consumption depends on the animal's age and degree of activity. Carbohydrates, that makes the remaining percentage, with two categories: specifically Structural (fibers), measures the amount of fiber in the hay ADF and NDF; and and Anonstructural carbohydrases, that include simple starch, water soluble carbohydrates (WSC), and ethanolsolube carbohydrates (ESC) make up the remaining percentages. The nonstructural carbohydrates measures the both types are technically fibers made of lignocellulosic compositions (hemicellulose, cellulose, lignin) [26]. The analysis done in this research study focuses on the percentage of carbohydrates in hay as it was the energy source in the experiment's samples. The microscopic image of the samples from the horse manure showed most of the fiber.

To evaluate the characteristics of the waste, it is important to predict the mass variation and the heat amount for manure during pyrolysis. In this report, the theoretical calculations for the mass variation during the pyrolysis process were attempted as the first step in conducting the theoretical analysis of the horse manure. At first, the overall kinetic reaction parameters and the Arrhenius equation were used to compare the experimental and the theoretical results. Then, while using the analytical model proposed by Miller and Bellan, the comparison between the experimental and the hypothetical results and the availability of the analytical model were evaluated.

In this study, the analytical model proposed by Miller and Bellan was used [36]. Figure 4 shows the concept of the chemical reaction process in the model. In this model, the composition of cellulose, hemicellulose, and lignin in the biomass are given as the calculation parameters, and the decomposition process for each composition is calculated using the reaction process. K_j is the reaction rate for each reaction process where the reaction rate can be found by using Eq. (2).

The parameters in the equation, such as A_j and E_j, were determined from the experimental results as shown in Table 2. Moreover, when the ACTIVE substance is converted to CHAR and GAS, the char formation mass ratios are 0.35, 0.60, and 0.75 for cellulose, hemicellulose, and lignin, respectively.

Table 1 Chemical compositions for dry hay with their percentage of availability [35]

Term	Meaning	Typical value
DM	Dry matter: the nutrients without water	85%
Moisture	The amount of water in the hay	11–16%
CP	Crude protein: the amount of protein in the hay	8–20%
ADF	Acid detergent fiber (cellulose + lignin): a measurement of the fiber	30–45%
NDF	Neutral detergent fiber (hemicellulose + cellulose + lignin): a measurement fiber	40–65%
NSC	Nonstructural carbohydrates: a measurement of simple sugar and starch the subset of this includes WSC, ESC, and NFC	5–25%
DE	Digestible energy: the amount of energy digested and used by the horse	0.75–1.0 Mcal/lb

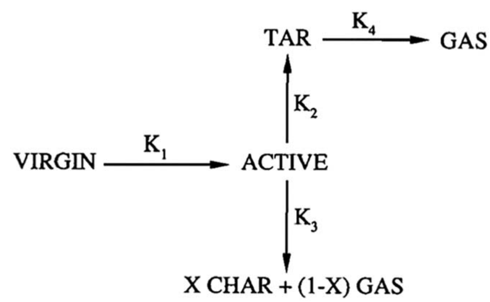

Fig 4 Reaction model [37]

Results

Experimental Results. The experiment was conducted using the DTG to run thermogravimetric and differential thermal analysis on horse manure with eight distinct heating rates starting from an ambient temperature of up to 1000 °C. The sample for each run came from a small amount of horse manure ranging between 10

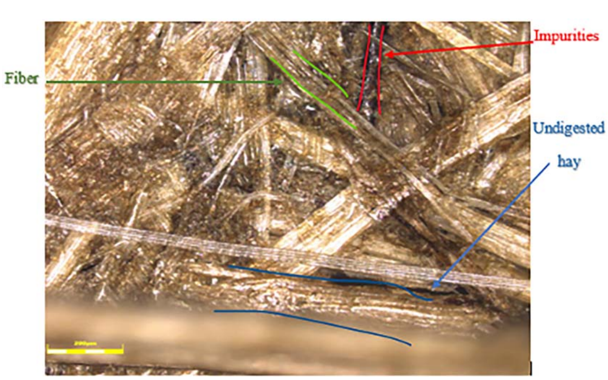

Fig 3 Macroscopic view of manure

Table 2 Components reduction parameters [36]

Reaction	A_j (1/s)	E_j (kJ/mol)	Source
k_1^c	2.8×10^{19}	242.4	Di Blasi and Russo (1994)
k_2^c	3.28×10^{14}	196.5	Di Blasi and Russo (1994)
k_3^c	1.3×10^{10}	150.5	Di Blasi and Russo (1994)
k_1^h	2.1×10^{16}	186.7	Ward and Braslaw (1985)
k_2^h	8.75×10^{15}	202.4	Di Blasi and Russo (1994)
k_3^h	2.6×10^{11}	145.7	Di Blasi and Russo (1994)
k_1^l	9.6×10^{8}	107.6	Ward and Braslaw (1985)
k_2^l	1.5×10^{9}	143.8	Koufopanos et al. (1989)
k_3^l	7.7×10^{6}	111.4	Koufopanos et al. (1989)
k_4	4.28×10^{6}	108.0	Di Blasi and Russo (1994)

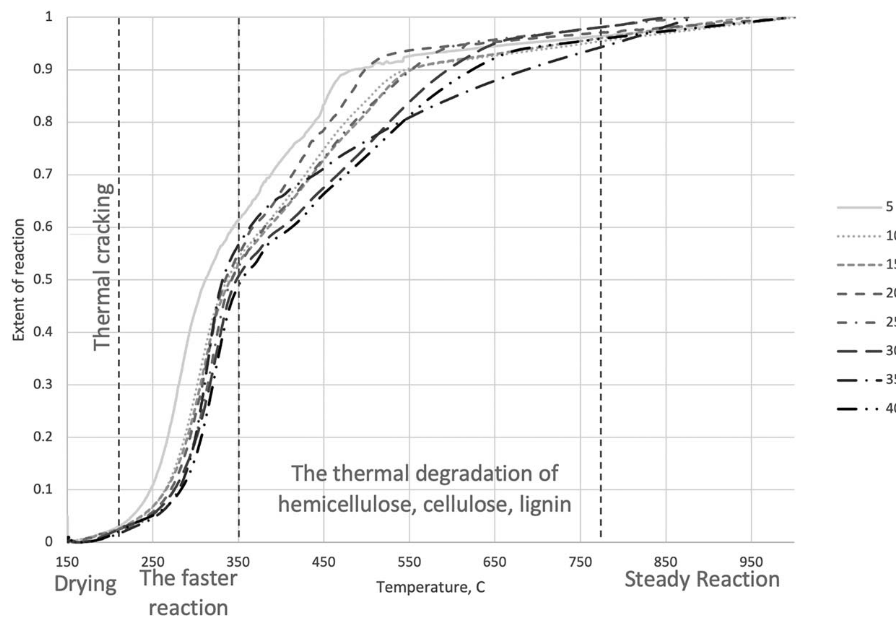

Fig 5 The extent of reaction for horse manure at different heating rates

and 30 mg collected from the same animal from a farm in Wisconsin. For the pyrolysis technique, the agent gas utilized in the experiment is nitrogen with the absence of oxygen. Figure 5 shows the horse pyrolysis extent of reaction curves for the eight different heating rates: 5, 10, 15, 20, 25, 30, 35, and 40 °C/min. The device starts collecting data at 150 °C instead of at room temperature. From room temperature to 150 °C, the previous interval is for drying the sample and for moisture evaporation since the sample is utilized immediately after it is taken out of the freezer containing frozen water. To achieve better results, the sample must be preheated to dry it; this process is called torrefaction where the biomass is heated to around 300 °C for a dry sample [37]. Data collection on a dry sample provides more accurate results and prevents fluctuation, specifically in the mass change. The collected data is only taken after the moisture evaporation phase, meaning at the temperature of 150 °C. At this temperature, the initial mass is at the maximum and the extent of the reaction is 0. At the temperature of 1000 °C, the final mass is at its minimum and the extent of the reaction is equal to 1, meaning no further reaction can be achieved [38]

From the graph, it is observed that all the curves follow the same trend with different latencies. There are four main stages of the pyrolysis reaction that can be identified. The first stage is for thermal cracking, which takes place starting at 200 °C. The second stage is for the faster reaction with a higher slope in a temperature range between 200 °C and 350 °C for the hemicellulose and cellulose mass degradation. The third stage, between 350 °C and 780 °C, is for thermal degradation of hemicellulose, cellulose, and lignin. The fourth stage after 780 °C is for a steady reaction. It is also observed that at the temperature of 490 °C and

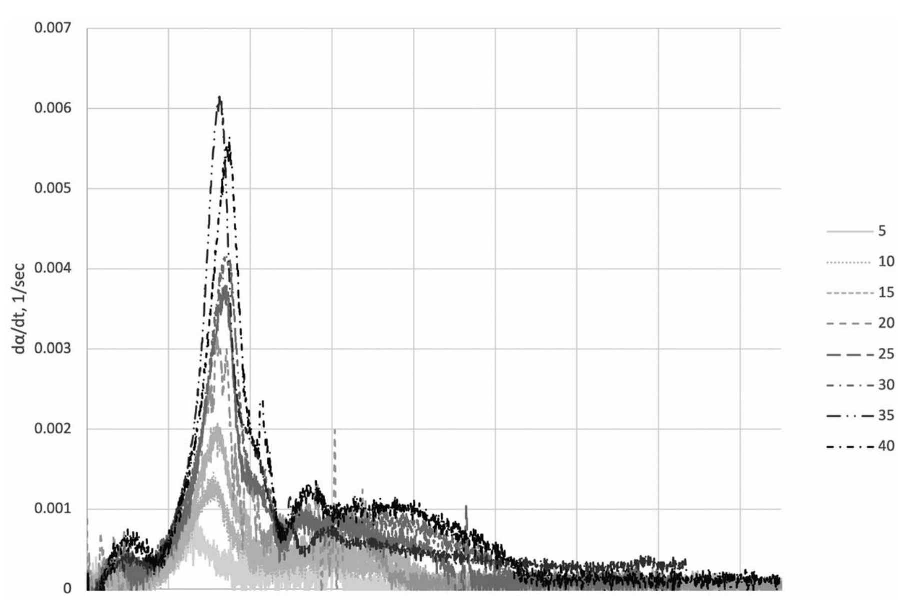

Fig 6 Rate of change of the extent of reaction

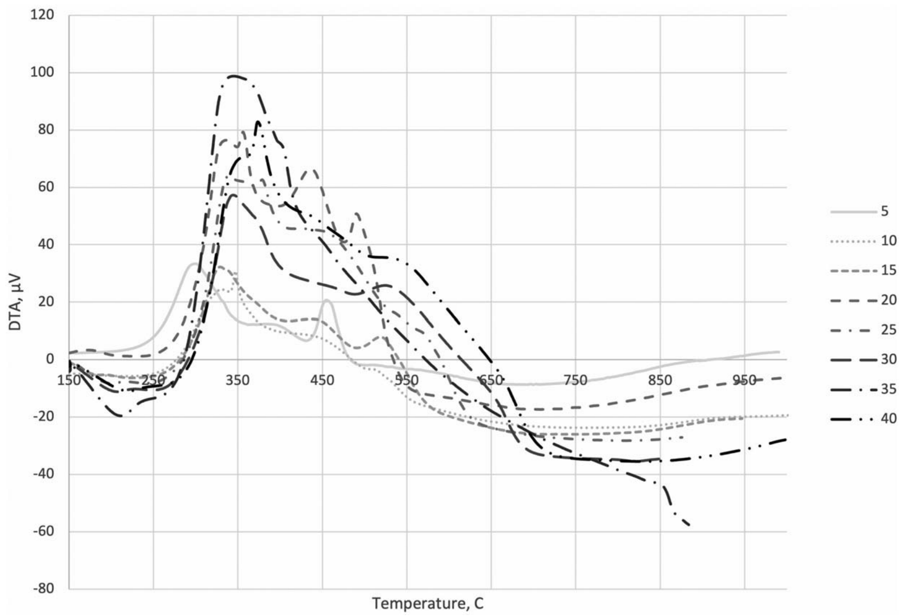

Fig 7 Rate of change of DTA with temperature

a heat rate of 5 °C/min, 90% of the reaction is completed, and 90% of the initial mass is decomposed.

Figure 6 is a graph that shows the rate of change of the extent of the reaction. The eight curves follow a similar trend with a delay in different heating rate peaks. The peaks represent the mass degradation due to the thermal cracking of the chemical compounds that make up the composition of the horse manure. Since horse manure is dominantly made of hay, the displayed results in the graph are expected. Two main peaks in the graph represent the thermal degradation of the sample's main organic composition: cellulose and hemicellulose while there is a small amount of lignin in

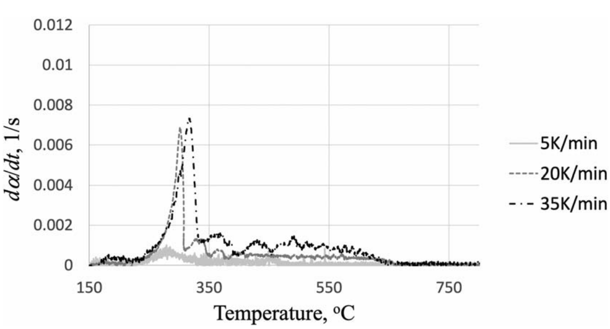

Fig 8 The experimental rate of extent of reaction for horse manure

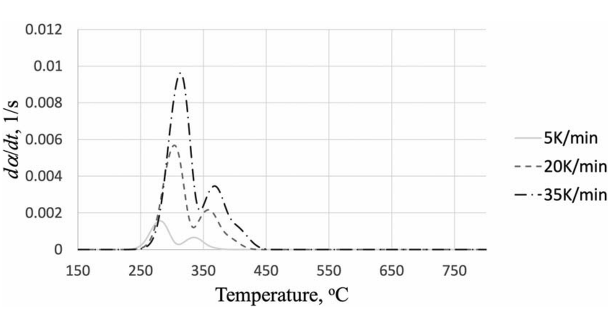

Fig 9 The theoretical rate of extent of reaction for horse manure

the sample as shown in the graph with a very small peak at higher temperatures. The first peak for the eight different rates represents hemicellulose and cellulose thermal degradation, which occurs at 270 °C and 335 °C. For the heating rate of 5 °C/min peak, hemicellulose and cellulose thermal degradation occurs at the temperature of 270 °C. The second peak to appear moving to the right is for the 10 °C/min heating rate, where the thermal degradation occurs at the temperature of 286 °C. The next peak is for the 15 °C/min heating rate, where thermal degradation occurs at the temperature of 293 °C. The remaining curves follow a similar pattern with a shift toward the right in the thermal degradation temperature due to the increase in the heating rate. The trend represented by the 35 °C/min shows a slightly different behavior in which the peak is at a lower temperature than it was expected, meaning that thermal degradation occurs at a lower temperature. This means that there was enough time for the heat transfer to allow the reaction to be completed. Even though the 35 °C/min peak is expected to occur at a higher temperature, it occurs in this experiment at the same temperature as the 15 °C/min. Also, the peak's magnitude is expected to be lower than the one at 40 °C/min. After an investigation into the raw data, it was noticed that the sample associated with the heating rate of 35 °C/min had the highest mass. All the other seven samples fell under the same range of mass after drying the manure except for the sample of 35 °C/min where it was more than double. The peak still appears at the expected range of temperature and this slight change is due to the faster reaction because of the adequate availability of mass. In conclusion, increasing the heating rate delays the thermal degradation of the sample composition due to the lack of time for a complete reaction.

Figure 7 shows the DTA variation with the temperature for the eight heating rates. According to the figure, all the heating rates follow a similar pattern in terms of the number of peaks and the temperature range of peaks with small peak variations. Notably, the trends are exothermic in a specific range of temperatures and endothermic in the rest. The 5 °C/min curve is the most stable among the eight different curves and is the curve with the widest range of temperature of positive energy from 150 °C to 490 °C. 10 °C/min and 15 °C/min are also stable; however, they have a smaller range of endothermic temperature. The sharp decline after the first peak implies higher heating rates where the reaction switches to an endothermic reaction. In conclusion, the reaction is most self-sustainable with a heating rate of 5 °C/min at a range of temperature up to 490 °C.

Mathematical Results. This code can be used for any animal manure or all types of waste, whereas the numerical results cannot factor in the effects of the impurities. However, the theoretical results are similar to the experimental results. Figure 8 is the graph for the experimental results for three different heating rates. Three random heating rates were picked: 5 °C/min, 20 °C/min, and 35 °C/min, and their trends from Fig. 6 are compared in a new graph with a theoretically generated graph. Figure 9 is the graph for the theoretical results using the Miller model and the code to generate the curves for the same mass and heating rates. It can be noted that the curves in both graphs follow the same trend, which could be used to validate experimental data. As explained previously in the results, the peaks represent the cellulosic bonds, including hemicellulose and cellulose bonds, which occur in both experimental and theoretical graphs. The theoretical graph is clearer because it does not involve moisture evaporation or impurities in the sample.

Conclusion

This research study is to investigate the effect of the heating rate of thermal cracking of the horse manure composition. The process conducted was pyrolysis, where only nitrogen was used as a gas agent along with a temperature range between room temperature and up to 1000 °C. Eight different heating rates were used, from 5 °C/min to 40 °C/min with 5 °C increments. Increasing the heating rate in pyrolysis causes latency in the reaction due to the lack of time to complete the reaction. This leads to latency in the thermal degradation of the sample compositions: hemicellulose, cellulose, and lignin. Regarding endothermic and exothermic reactions, the most stable curves are 5, 10, and 15 °C/min. However, the most self-sustainable heating rate is 5 °C/min, which allows enough time for the reaction to be completed. The slowest heating rates allow enough time for a complete reaction and do not cause latency in peaks and higher spikes; rather they provide gradual increases in energy. However, these slow processes use more energy in the furnace because they have a longer operating time to achieve a similar amount of energy. From the graphs, small peaks in higher temperatures represent the mass degradation due to the lignin composition. Horse manure consists of a higher percentage of hemicellulose and cellulose and a significantly smaller amount of lignin. Energy is released because of the thermal cracking of biomass chemical compositions due to the adequate amount of heat applied. Different types of animal manure require distinct temperatures for the bonds of the compounds to break down into more simple chemical molecules known as syngas. For instance, horse manure requires a relatively low amount of heat for the cellulosic thermal cracking to be achieved. Horse manure consists of a negligible amount of lignin, which means all the energy from horse manure is released from the thermal cracking of cellulosic bonds. The potential for higher energy continuity is achieved by combining the different animal manure types and is linked to the different thermal cracking temperatures for lignocellulosic bonding. The experimental results for the thermal degradation of the cellulose and hemicellulose are validated using the mathematic model from Miller and Bellan, which was used to develop a code that could be used to predict the mass and heat analysis for the pyrolysis process with different parameters and different organic animals.

Conflict of Interest

There are no conflicts of interest.

Data Availability Statement

The datasets generated and supporting the findings of this article are obtainable from the corresponding author upon reasonable request.

Nomenclature

k = the constant rate of the reaction
n = order of reaction
t = time
J = Joules
A = preexponential constant in Arrhenius equation
E = energy
K = reaction rate
M = mass
W = mass of biomass
E_a = energy of activation
ADF = acid detergent fiber
Btu = British thermal unit
CP = crude protein
DM = dry matter
DE = digestible energy
DTA = differential thermal analysis
DTG = differential thermal gravimetry
NDF = neutral detergent fiber
NSC = nonstructural carbohydrates
TGA = thermogravimetric analysis

Greek Symbols

α = extent of reaction
β = linear heating rate
ρ = density
Δ = change

References

[1] U.S. Renewable Energy Factsheet, "Center for Sustainable Systems, https://css.umich.edu/publications/factsheets/energy/us-renewable-energy-factsheet, Accessed September 21, 2023.
[2] U.S. Energy Information Administration—EIA—Independent Statistics and Analysis, U.S. Energy Facts Explained – Consumption and Production – U.S. Energy Information Administration (EIA), https://www.eia.gov/energyexplained/usenergy-facts/, Accessed October 21, 2023.
[3] Bentsen, N. S., Felby, C., and Thorsen, B. J., 2014, "Agricultural Residue Production and Potentials for Energy and Materials Services," Prog. Energy Combust. Sci., **40**, pp. 59–73.
[4] U.S. Energy Information Administration—EIA—Independent Statistics and Analysis, U.S. Energy Facts Explained – Consumption and Production – U.S. Energy Information Administration (EIA), https://www.eia.gov/energyexplained/us-energy-facts/, Accessed October 21, 2023.
[5] U.S. Energy Information Administration – EIA– Independent Statistics and Analysis, U.S. Energy Facts Explained – Consumption and Production, https://www.eia.gov/energyexplained/us-energy-facts/, Accessed October 21, 2023.
[6] U.S. Energy Information Administration – EIA– Independent Statistics and Analysis, https://www.eia.gov/energyexplained/us-energy-facts/, Accessed October 21, 2023.
[7] U.S. Energy Information Administration – EIA– Independent Statistics and Analysis, https://www.eia.gov/energyexplained/us-energy-facts/, Accessed October 21, 2023.
[8] Hussein, M. S., Burra, K. G., Amano, R. S., and Gupta, A. K., 2017, "Effect of Oxygen Addition in Steam Gasification of Chicken Manure," Fuel, **189**, pp. 428–435.
[9] Admin, L., 2020, *Liquid Manure Storage Ponds, Pits, and Tanks*, Livestock and Poultry Environmental Learning Community, across the U.S. (and Canada).
[10] Hoffman, B., 2014, *What the Pork? China, Pigs and Poop*, Forbes, New Jersey.
[11] Cross, P., 2017, *The Great Manure Crisis of 2017*, HiPoint Agro. Bedding Crop.
[12] FAOSTAT, 2016, Livestock Primary. http://www.fao.org/faostat/en/#data/QL.
[13] Reid, A., 2015, *Palm Beach County Struggling to Deal With Horse Waste*, A. Reid, ed., SunSentinel, Florida.
[14] Brethauer, S., and Studer, M. H., 2015, "Biochemical Conversion Processes of Lignocellulosic Biomass to Fuels and Chemicals—A Review," CHIMIA, **69**(10), p. 572.
[15] "How Does Anaerobic Digestion Work?," 2024, US EPA. https://www.epa.gov/agstar/how-does-anaerobic-digestion-work.
[16] Khalid, A., Arshad, M., Anjum, M., Mahmood, T., and Dawson, L., 2011, "The Anaerobic Digestion of Solid Organic Waste," Waste Manage., **31**(8), pp. 1737–1744.
[17] Stuart, P., 2006, *The Advantages and Disadvantages of Anaerobic Digestion as a Renewable Energy Source*, Loughborough University, Loughborough.
[18] Evangelisti, C., Bossola, F., and Dal Santo, V., 2017, "Catalysts for Hydrogen Production From Renewable Raw Materials, Byproducts and Waste," Hydrogen Prod. Sep. Purif. Energy, pp. 71–101.
[19] Knothe, G., Krahl, J., and Gerpen, J. V., 2010, *The Biodiesel Handbook*, Elsevier Science.

[20] Amano, R. S., and Hussein, M. S. I., 2020, "," "Study of Biofuel Animal Manure," *Innovations in Sustainable Energy and Cleaner Environment*, A. K. Gupta, A. De, S. K. Aggarwal, A. Kushari, and A. Runchal, eds., Springer, Singapore.
[21] Lundgren, J., and Pettersson, E., 2009, "Combustion of Horse Manure for Heat Production," Bioresour. Technol., **100**(12), pp. 3121–3126.
[22] Da Lio, L., Castello, P., Gianfelice, G., Cavalli, R., and Canu, P., 2021, "Effective Energy Exploitation From Horse Manure Combustion," Waste Manage., **128**, pp. 243–250.
[23] Kumar, A., Jones, D., and Hanna, M., 2009, "Thermochemical Biomass Gasification: A Review of the Current Status of the Technology," Energies, **2**(3), pp. 556–581.
[24] Mallick, D., Buragohain, B., Mahanta, P., and Moholkar, V. S., 2017, "Gasification of Mixed Biomass: Analysis Using Equilibrium, Semi-Equilibrium, and Kinetic Models," Coal Biomass Gasification, **17**(1), pp. 223–241.
[25] Hussein, M. S., Burra, K. R., Amano, R. S., and Gupta, A. K., 2017, "Temperature and Gasifying Media Effects on Chicken Manure Pyrolysis and Gasification," Fuel, **202**, pp. 36–45.
[26] Amano, R. S., and Hussein, M. S., 2016, "Simultaneous Differential Thermal and Thermogravimetric Analysis of Chicken Manure Gasification Using Nitrogen and Carbon Dioxide," 2016 AIAA Propulsion and Energy, Salt Lake City, UT, July 25–27.
[27] Amano, R., Ibrahim, M., and Gupta, A., 2013, "Experimental Investigation of Gasification of Biomass Using Carbon Dioxide," 51st AIAA Aerospace Sciences Meeting, Including the New Horizons Forum and Aerospace Exposition, Grapevine, TX, Jan. 7–10.
[28] Burra, K. R., Hussein, M. S., Amano, R. S., and Gupta, A. K., 2017, "Syngas Evolutionary Behavior During Chicken Manure Pyrolysis and Air Gasification," Appl. Energy, **181**, pp. 408–415.
[29] Trninic, M., Stojiljkovic, D., Jovovic, A., and Jankes, G., 2016, "Biomass Gasification Technology: The State of the Art Overview," 2016 Fourth International Symposium on Environmental Friendly Energies and Applications (EFEA), Belgrade, Serbia, Sept. 14–16, pp. 1–8.
[30] Fernandez-Lopez, M., Pedrosa-Castro, G. J., Valverde, J. L., and Sanchez-Silva, L., 2016, "Kinetic Analysis of Manure Pyrolysis and Combustion Processes," Waste Manage., **58**, pp. 230–240.
[31] Selim, O. M., and Amano, R. S., 2021, "Co-Pyrolysis of Chicken and Cow Manure," ASME J. Energy Resour. Technol., **143**(1), p. 011301.
[32] Selim, O. M., Hussein, M. S., and Amano, R. S., 2020, "Effect of Heating Rate on Chemical Kinetics of Chicken Manure With Different Gas Agents," ASME J. Energy Resour. Technol., **142**(10), p. 102104.
[33] Westendorf, M, 2004, *Horses and Manure*, Equine Science Center, New Brunswick, NJ.
[34] Zongliu, 2017, "Manure to Energy: Understanding Processes, Principles and Jargon," Texas Animal Manure Management Issues. https://tammi.tamu.edu/2017/07/17/manure-energy-understanding-processes-principles-jargon/.
[35] U.S. Energy Information Administration – EIA– Independent Statistics and Analysis, https://www.eia.gov/energyexplained/us-energy-facts/, Accessed October 21, 2023.
[36] Miller, R. S., and Bellan, J., 1997, "A Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicellulose and Lignin Kinetics," Combust. Sci. Technol., **126**(1–6), pp. 97–137.
[37] "Biomass Energy," Education. https://education.nationalgeographic.org/resource/biomass-energy/.
[38] Selim, O. M., Maache, M., Kada, C., Kumano, H., and Amano, R., 2023, "Thermochemical Conversion of Cow Manure With Different Heating Rates," ASME Power Appl. R&D, **2023**(108750), pp. 1–6 .