Thermal Investigation and Kinetic Modeling of Lignocellulosic Biomass Combustion for Energy Production and Other Applications

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ABSTRACT: Herein, we studied the combustion and pyrolysis for Miscanthus × giganteus (elephant grass) using thermal gravimetric and differential scanning calorimetry techniques. Currently, miscanthus is used to an extent in energy generation applications; however, issues regarding its physicochemical combustion characteristics currently hinder this uptake. In this work, the thermal and kinetic analyses of dry miscanthus and its char were performed to obtain a better understanding of its physicochemical combustion characteristics and consequently to achieve the highest benefit from the combustion process. Different kinetic modeling has been used to calculate the activation energy and the kinetic parameters during combustion/pyrolysis, such as ASTM-E698, Flynn-Wall and Ozawa, and differential iso-conversional methods. It was observed that the activation energy values were 22.3, 40−150, and 40−165 kJ mol−1 for miscanthus, respectively. Furthermore, miscanthus species were tested in wastewater treatment and showed a potential for the rapid removal of cadmium heavy metal. In addition, a study of miscanthus ash was performed and indicated that it can be used as a source of potassium in the fertilizer industry.

1. INTRODUCTION

The global demand for energy is growing, and it is expected to increase by about 50% during the next two decades and projected to reach around 778 EJ by 2035, which represents a great challenge for all countries.1 Fossil fuels, including coal, natural gas, crude oil, and its derivatives, still represent the primary energy source worldwide. Fossil fuel reserves are, however, limited and will soon come to an end2−4 while burning them will continue to cause serious environmental and health concerns.5−7 An important candidate for meeting future energy demands sustainably is biomass which can be converted into liquid biofuel or a solid energy carrier.2,6−11 In 2007, the European Union set a target of increasing its share from renewable energy sources to 20% of the EU total energy consumption by 2020, which is a part of the 20−20−20 target with the combined reduction of EU greenhouse gas emissions to 20% and improvement in the EU’s energy efficiency by 20% on 1990 levels.12 In Europe, biomass is the main feedstock for renewable energy production as required by the EU commission.13

Five basic categories of biomass materials are used for the production of biofuel and solid energy carrier including energy crops, virgin wood, agricultural residues, food wastes, and industrial wastes and coproducts.2,14 The energy crop category is considered to be the most important biomass group for bioenergy production. These are nonfood crops rich in lignocellulose which make good raw material for the production of heat and electricity, biofuels, or biomaterials.15−21 Among all the nonfood energy crops, miscanthus is considered to be a suitable bioenergy source as a result of its ability to grow in more marginal soils and climate conditions, while also requiring relatively low maintenance and providing a high yield/energy content ratio.15,22 Miscanthus is a perennial rhizomatous lignocellulosic crop with the C4 photosynthetic pathway.23 Since the 1980s, miscanthus has been considered as a promising energy crop in Europe with its current use being mainly for the production of heat and electricity.7,24−25 Miscanthus × giganteus, the most popular species, is currently farmed in Europe for electricity and heat generation in combined heat and power (CHP) plants and to a smaller degree as a feedstock for biofuels production.

The energy stored in miscanthus, as biomass, can be extracted in various ways; however, most require a pretreatment step.26,27 Two main technologies used for the conversion of lignocellulosic biomass are thermochemical and biochemical
technologies. Biochemical conversion can occur by either digestion or fermentation, while thermo-chemical conversion can occur by four different technologies:

(i) Combustion, which is the burning of biomass in air within a temperature range of 800–1000 °C to produce hot gases and ash and consequently converting the stored chemical energy into heat, kinetic, and thus electrical energy.

(ii) Gasification, in which the biomass is exposed to partial oxidation at high temperatures (800–1500 °C) to convert it into a combustible gas mixture. The low-energy gas produced can be burnt directly or used as a fuel for gas engines and gas turbines, while the medium-energy gas can be used for the production of chemicals.

(iii) Pyrolysis, which is the conversion of biomass to solid, liquid, and gaseous fractions. Pyrolysis is the first physical-chemical step that takes place in all thermo-chemical reactors during combustion or gasification.

(iv) Liquefaction, which is the conversion of biomass into stable liquid hydrocarbons in low temperatures (200–400 °C) and high hydrogen pressures (2–20 × 10^9 Pa).

The direct combustion of miscanthus for electricity and heat generation represents the simplest and the main route for the valorization and its conversion to useful energy. Currently, miscanthus is used to an extent in energy generation applications; however, issues regarding its physicochemical combustion characteristics currently hinder this uptake. Therefore, studying the combustion behavior of miscanthus is crucial to further understand its physicochemical combustion characteristics and consequently to achieve the greatest benefit from the combustion process as a conversion method. For this purpose, a study of the thermal behavior and kinetic parameters during miscanthus combustion was carried out using thermal gravimetric (TG) and differential scanning calorimetry (DSC) techniques. The model-fitting and the iso-conversational methods can be applied to a series of DSC/TGA experiments at different heating rates to detect the kinetic data during the thermal combustion of miscanthus. The latter method is considered to be more accurate than the former one, which tends to produce highly unreliable values of kinetic parameters. Studying the thermal kinetics using the iso-conversational method allows the estimation of the activation energy as a function of conversion with no need for information about the reaction mechanism model. In addition, it can describe the kinetics of multistep processes during the combustion via a variation of the activation energy with the extent of conversion.

In the second part of our study, we propose a novel approach of new applications of miscanthus species. In addition to using Miscanthus × giganteus as an energy source, its biochar, produced by heating in the absence of air at ≈500 °C (pyrolysis), can be used as an effective soil improver. It has been found that miscanthus biochar is rich in phytoliths (SiO2·nH2O), a potentially bioavailable silicon source, and as such Miscanthus × giganteus is a high Si accumulator plant. It is well-known that the common composition of fertilizers is N–P–K (nitrogen, phosphorus, and potassium). Finding a potassium source for the fertilizer industry is challenging. Potash can offer this K source; however, it is prone to humidity and has problems for typical agricultural fertilizer. We investigated the composition of miscanthus ash that remains after the combustion process to see if it can offer the K source for fertilizer composition. There is also a possibility of using dry miscanthus plant or its derivative biochar in heavy metal removal. In the literature, miscanthus biochar has been utilized in Cd removal from aqueous solutions, and it was reported that the pyrolytic temperature had a substantial effect on the surface structure and elemental properties of Miscanthus sacchariflorus biochar and that increasing the pyrolytic temperature increased the Cd removal. It is clear that certain properties of biochar including large specific surface area, porous structure, and mineral components make it a potentially effective adsorbent for the removal of pollutants from aqueous solutions.

To the extent of the authors’ knowledge, no research has been carried out on the potential use of such dry, unprocessed plant material for heavy metal removal.

A detailed comprehensive review was published by the ICTAC Kinetics Committee addressing the problems and reporting the essential principles that should be followed to obtain thermal analysis data that are adequate to the kinetic computations.

Herein, the combustion of dry miscanthus plant (DMP) and its biochar is studied using TGA/DSC techniques, and the iso-conversational method was used for the calculation of the kinetic parameters from DSC curves. Moreover, new potential applications for these miscanthus species for heavy metal removal and in the composition of fertilizer are proposed. To the best of the authors’ knowledge, this is the first detailed kinetic study along with the promising industrial applications of miscanthus species.

2. MATERIALS AND METHODS

2.1. Miscanthus Material Preparation. The miscanthus was harvested from a 10-yr-old energy crop grown at the Agri-Food and Biosciences Institute (AFBI), Environment & Renewable Energy Centre, Hillsborough, Northern Ireland (54.453077, −6.086162). The site was formerly long-term grass pasture on Surface Water Gley (Class 1) soil type (Avery, 1980) overlying shale. The plantation has been harvested in February each year after winter senescence using a fine-chop Kemper head harvester; the chopped raw fuel was blown into a tractor-drawn silage trailer, drawn off, and tipped into a forced air drying bay. Sampling was carried out using British Standards methods; solid biofuels sampling BS EN14778:2011 and particle size distribution BS EN 15149:1-2010. Grab samples were collected randomly from each load and combined to form a bulk sample for moisture content, performed according to the oven drying method (BS EN 14774-3:2009) with samples subdivided, placed into a drying oven (Gallenkamp) for 48 h at 80 °C, and dried until a constant final weight. The miscanthus fuel used herein had the same chain of custody after their receipt in a dry and crushed form.

2.2. Cadmium Heavy Metal Solution Preparation. The cadmium heavy metal solution was prepared by dissolving an appropriate amount of Cd(NO3)2·2H2O in deionized water to get the final desired Cd concentration of 100 mg L−1. The appropriate amount of dry miscanthus plant (DMP) or its biochar was subsequently placed in a bottle containing the Cd heavy metal solution. Water samples were taken after an hour then at different time intervals, i.e., 1, 3, and 7 days, to be
analyzed by the inductively coupled plasma optical emission spectrometry (ICP-OES) that was used to determine the Cd metal concentration in the absorption tests. The Cd solution was analyzed with an ICP optical emission spectrometer (Optima 4300 DV, PerkinElmer).

2.3. Miscanthus Characterization. Brunauer−Emmett−Teller (BET) analysis was performed using a Micromeritics ASAP 2020 system. BET surface area and pore volume were measured by N2 adsorption and desorption isotherms at liquid nitrogen temperature (−196 °C).

Compositions of the DMP were characterized by means of proximate and ultimate analyses. Elemental (C, H, and N) analysis was performed using a PerkinElmer PE2400 CHNS/O Elemental Analyzer. The oxygen content was calculated by difference from the data obtained by a PerkinElmer PE2400 CHNS/O Elemental Analyzer. Proximate analysis was carried out according to the ASTM method to determine the percent of moisture (ASTM Standard D2867-95), volatile matter (ASTM Standard D5832-95), ash content (ASTM Standard D2866-94), char, and fixed carbon (by difference). Char and volatile contents were determined using thermogravimetric analysis (TGA), with heating to 900 °C at a rate of 10 °C min−1 and holding the temperature for 10 min to ensure constant final weight. Again with the TGA, % ash was obtained by heating to 500 °C with a heating rate of 10 °C min−1 then heating to 575 °C with 2.5 °C min−1 and holding for 10 min.

Scanning electron microscopy (SEM) was carried out on a FEI Quanta 250 FEG MKII with a high-resolution environmental microscope (ESEM) using XT Microscope Control software and linked to an energy-dispersive X-ray (EDX) detector. Two types of detectors were used in SEM analysis: the Everhart−Thornley detector (ETD) which is used to detect secondary electrons emitted from the sample, and the backscattered electron detector (BSED), which is used to measure the backscattered electrons from the sample, where the elements of higher atomic number appear brighter in the image due to emitting a large number of backscattered electrons (BSEs). The EDX used was a 10 mm2 silicon drift detector (SDD)-x-act from Oxford Instruments which utilizes Aztec EDS analysis software. Both systems used the same chamber.

TGA was performed at a specific heat range with different heating rates of 2.5, 10, 20, and 30 °C min−1, in a stream of dry N2 flowing at 40 cm3 min−1, using a simultaneous thermal analysis Mettler Toledo (TGA/DSC) thermogravimetric analyzer Pyris TGA/DSC1. Changes in mass of the sample were recorded during the ramping operation. DSC was used to determine the heat liberated in watts per gram. For the kinetic modeling, the weights of the samples were between 4.93 and 4.97 mg to reduce the effect of heat and mass transfer on the data obtained from the DSC instrument. Prior to the DSC experiments, the instrument was calibrated using indium as reference standard. The TGA instrument was also calibrated for buoyancy effects to allow quantitative estimation of weight changes. Experiments were performed twice to ensure reproducibility, and the standard error was found to be ±1 °C.

3. RESULTS AND DISCUSSION

3.1. Miscanthus Characterization. 3.1.1. FTIR Analysis. The Fourier transform infrared (FTIR) spectra of the DMP in the wavenumber range of 2500–4000 cm−1 are shown in Figure 1. The inset reports two absorption bands at 2918 and 2849 cm−1 which are attributed to the C−H stretching of cellulose and lignin, respectively.

3.1.2. Thermogravimetric Data. The percentage composition of the cellulose, hemicellulose, and lignin in the lignocellulosic biomass are in the range of 40–60, 20–40, and 10–25 wt %, respectively, and the values previously reported for miscanthus are 41, 30, and 22%, respectively.

The complete and partial combustion of hemicellulose produces CO2 and CO gases, respectively. The emission of these gases is due to the pyrolysis of the carboxylic groups in
the unbranched structure of saccharides (xylose, mannose, glucose, galactose, etc.) which are easily removed during pyrolysis. There is usually a complete combustion of hemicellulose which emits CO₂ and water vapor. In contrast, the pyrolysis of cellulose, which contains OH and C−O groups, emits mainly CO which comes from the pyrolysis of the unbranched long polymers of glucose, and consequently cellulose decomposes at a higher temperature than hemicellulose, meaning complete combustion is more difficult to achieve. Lignin, however, is the only component which is responsible for emitting H₂ and CH₄ gases during pyrolysis, and this is due to the pyrolysis of the branched aromatic rings and methoxyl groups (−O−CH₃) which are, therefore, even more difficult to decompose.

3.1.3. DSC at High Heating Rates. The DSC curves of DMP at different heating rates (i.e., 2.5, 10, 20, and 30 °C min⁻¹) under air atmosphere are shown in Figure 2. It is not surprising that with increasing the heating rates, a shift toward higher peak decomposition was observed. The ignition and burnout temperatures along with the heat liberated at different heating rates were calculated from the DSC curves and are presented in Figure 3 and Table S2. The ignition temperature logically increased with increasing heating rates, and this is in agreement with Figure 2 and the work done by Kok and Ozgur. The burnout temperature increased by 75 °C with increasing the heating rate from 2.5 to 10 °C min⁻¹. However, a slight increase was observed with increasing the heating rate from 10 to 30 °C min⁻¹. The heat liberated during the DMP combustion increased by 4625 W g⁻¹ with increasing the heating rate from 2.5 to 30 °C min⁻¹.

Figure 4 reports the DSC pyrolysis curves of DMP at different heating rates of 2.5, 10, 20, and 30 °C min⁻¹ under N₂ atmosphere in order to investigate the pyrolysis of miscanthus. Clearly, the endothermic peak at 80 °C is ascribed to the dehydration process in the DMP samples. The small endothermic peak appearing at 140 °C is attributed to the decomposition of the first component (hemicellulose), followed by broad exothermic pyrolysis peak of the mixture of three principal constituents that shifted to higher temperature with increasing heating rate from 2.5 to 30 °C min⁻¹. The lignin pyrolysis decomposition peaks appeared at 660, 700, and 734 with heating rates of 10, 20, and 30 °C min⁻¹, respectively. These results are in a line with the work reported by Le Brech et al., and a distinguishing lignin pyrolysis peak at around 700 °C was described by Yang et al. Alvarez et al. studied the combustion of 28 common biomass types, including miscanthus, and they reported that miscanthus showed two temperature ranges of combustion of 240–340 and 450–550 °C using the DTG data. Furthermore, they found that the combustion characteristics of the lignocellulosic biomass are about the same; thus, they proposed the two steps of the kinetic reaction are

\[ X(\text{solid}) \rightarrow Y(\text{solid}) + G1(\text{gas}) \text{ Step 1} \]
\[ Y(\text{solid}) \rightarrow A(\text{ash}) + G2(\text{gas}) \text{ Step 2} \]

It is well-known that the gross calorific value (GCV) or the higher heating value (HHV) of fossil fuel (e.g., coal) is higher than that of lignocellulosic biomass due to the latter having less fixed carbon, more volatile matter, and more oxygen and consequently lower GCV. For instance, the average GCV of coal is 20 120 kJ kg⁻¹, while it is lower in the case of dry biomass such as wood and bagasse with 14 644 and 18 410 kJ kg⁻¹, respectively. The GCV of DMP was calculated to be 16 600 kJ kg⁻¹, typical among lignocellulosic biomass species.
used for energy generation. To improve the combustibility of miscanthus, “smoldering combustion” is recommended. Typically, upon heating of biomass, it dries and pyrolyzes, and in the presence of O₂, ignition takes place through flaming (gas-phase homogeneous combustion) or smoldering (heterogeneous combustion). Smoldering is the combustion of porous fuels via a slow, flameless, and low-temperature burning process, considered to be the most continuous and feasible type of combustion. There are many factors affecting the calorific value of the biomass such as its composition, ash content, volatile matter, cultivation technique, fertilizer utilized, soil composition, and atmospheric weather conditions. Recently, Huang and Rein studied the possible mechanisms of smoldering combustion during the thermochemical conversion of biomass in detail. There are three common schemes that can describe the reaction mechanism; the first drying step is the common step between all these mechanisms, as shown below:

1. Three-step mechanism
   - (a) Biomass·H₂O → Biomass + H₂O
   - (b) Biomass → γ-Char + Pyrolysis gas
   - (c) γ-Char + O₂ → γ-Ash + Gas
   where γ-char is the char produced during the biomass pyrolysis and γ-ash is the ash produced during the smoldering combustion. This is the typical three steps, which are (a) drying, (b) pyrolysis, and (c) combustion.

2. Five-step mechanism
   - (a) Biomass·H₂O → Biomass + H₂O
   - (b) Biomass → γ-Char + Pyrolysis gas
   - (c) Biomass + O₂ → ϕ-Char + Gas
   - (d) γ-Char + O₂ → γ-Ash + Gas
   - (e) ϕ-Char + O₂ → ϕ-Ash + Gas
   where γ-Char and ϕ-Char are different chars produced during the parallel pyrolysis and oxidation, followed by the oxidation of these chars in the combustion steps (d, e) resulting in the γ-Ash and ϕ-Ash.

3. Nine-step mechanism
   - (a) Biomass·H₂O → Biomass + H₂O
   - (b) Hemicellulose → hpγ-Char + hp-Gas
   - (c) Cellulose → cpγ-Char + cp-Gas
   - (d) Lignin → lpγ-Char + lp-Gas
   - (e) Hemicellulose + O₂ → hϕγ-Char + Gas
   - (f) Cellulose + O₂ → cϕγ-Char + Gas
   - (g) Lignin + O₂ → lϕγ-Char + Gas
   - (h) (hp, cp, lp)γ-Char + O₂
     → (hp, cp, lp)ϕ-Char + O₂
   - (i) (hp, cp, lp)ϕ-Char + O₂
     → (hp, cp, lp)ϕ-Ash + Gas
   where hpγ-Char, cpγ-Char, and lpγ-Char are the chars produced during the pyrolysis of hemicellulose, cellulose, and lignin, respectively; hϕγ-Char, cϕγ-Char, and lϕγ-Char are the oxidized forms of hemicellulose, cellulose, and lignin, respectively.

In this proposed mechanism, the three different components of biomass (hemicellulose, cellulose, and lignin) behave differently and separately, i.e., each component pyrolyzes producing the equivalent char (steps b, c, and d). At the same time, these components oxidize to produce different char compositions (steps e, f, and g). Finally, these different chars are oxidized in the combustion steps (h and i).

3.2. Kinetic Modeling. The activation energy and the pre-exponential factor in this study using the iso-conversional methods such as ASTM-E698 and Flynn-Wall–Ozawa and differential iso-conversional method such as the Friedman method.

Model-fitting and model-free (iso-conversional) are the two common methods for studying the DSC/TGA solid-state kinetic data. The model-fitting method is based on the best
fitting of the thermogravimetric data with the different models using a single DSC/TGA curve. However, this method has drawbacks as the thermogravimetric data might fit with more than one model or give higher kinetic parameter values. On the other hand, the iso-conversional method has advantages over the model-fitting method due to its simplicity and the elimination of error related to the model fitting. Different heating rate curves are required to calculate the kinetic parameters in the iso-conversional method as a function of the conversion (α), i.e., E_a calculated for each conversion point. It is well-known that the thermal analysis mechanism is complicated as it tends to take place in multiple steps with different reaction rates, and as such an iso-conversional method is the most suitable method and commonly used in this case. The Kissinger method is the only model-free method that does not detect the E_a as a function of progressive conversion (α), so it is not considered as an iso-conversional method assuming a constant E_a.

The basic principles of model-free (iso-conversional) method are outlined below.

The rate of thermal decomposition of miscanthus can be described in terms of conversion (α) and temperature (T) as in eq 1:

\[
\frac{da}{dt} = k(T)f(\alpha)
\]

where α can be expressed as the decomposed mass fraction of miscanthus as in eq 2

\[
\alpha = \frac{m_i - m_f}{m_i - m_0}
\]

where m_0, m_i, and m_f are initial, actual, and final masses, respectively.

The Arrhenius equation describes the temperature-dependent function in terms of the activation energy (E_a) and the pre-exponential factor (k_0) as in eq 3.

\[
k(T) = k_0e^{(-E_a/RT)}
\]

where E_a is the activation energy in kJ mol\(^{-1}\), T the absolute temperature in Kelvin, R the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), and k_0 the pre-exponential factor (min\(^{-1}\)).

When eqs 1 and 3 are combined, the thermal decomposition equation of miscanthus can be expressed as in eq 4.

\[
\frac{da}{dt} = k_0e^{(-E_a/RT)}f(\alpha)
\]

In the nonisothermal iso-conversional method, using different linear heating rates (β = dT/dt), the thermal decomposition equation can be expressed as in eq 5

\[
\frac{da}{dT} = \frac{k_0}{\beta}e^{(-E_a/RT)}f(\alpha)
\]

3.2.1. Nonisothermal Iso-conversional Methods.

3.2.1.1. ASTM-E698 Method. This method is suitable for a single-step reaction and can be presented as in eq 6.

\[
\frac{\beta da}{dt} = k_0e^{(-E_a/RT)}(1 - \alpha)
\]

3.2.1.2. Flynn-Wall and Ozawa Method. The previous method is not quantitatively appropriate for multiple-step reactions such as autocatalytic reactions. The Flynn-Wall and Ozawa (FWO) method proposes the calculations of the variations of the apparent activation energy in terms of different linear thermogravimetric curves using the integral iso-conversional analysis method.\(^{57,58}\) The E_a can be calculated by plotting the natural logarithm of heating rates (ln β) versus 1000T\(^{-1}\) which represents a linear relationship with a given α at different heating rates as in eq 7.

\[
\ln\beta = \ln\left(\frac{k_0E_a}{Rg(\alpha)}\right) = 5.331 - 1.052\frac{E_a}{R\cdot T}
\]

where g(α) is constant at a given value of α.

3.2.1.3. Kissinger—Akahira—Sunose Method. In this method, the E_a can be calculated by plotting the natural logarithm of βT\(^{-1}\) versus the temperature inverse\(^{61}\) as shown in eq 8.

\[
\ln\beta T^{-1} = \ln\left[\frac{k_0T}{E_a g(\alpha)}\left(1 - \frac{2RT}{E_a}\right)\right] - \left(\frac{E_a}{R\cdot T}\right)
\]

3.2.2. Isothermal Iso-conversional Methods. 3.2.2.1. Isothermal Friedman Method. The Friedman method assumes that the thermal decomposition is independent of the temperature but dependent on the reaction progress (rate of the mass loss); hence, f(α) is constant at any given α. Taking the natural logarithm of both sides of eq 5 gives eq 9. Thus, by plotting ln β dα/dT versus the inverse temperature, E_a can be calculated from the slope E_a/R.

\[
\ln\beta \frac{d\alpha}{dT} = \ln[k_f(\alpha)] - \frac{E_a}{RT}
\]

DSC detects the heat flow of the reaction process during the isothermal experiments,\(^{59}\) that heat flow during the combustion of DMP under an air atmosphere with different heating rates is shown in Figures 6 and 7 (colored and black curves are for practical and theoretical data, respectively) along with Table 1. It is apparent that the decomposition temperature range was shifted toward a higher temperature range from 172–487 to 190–570 °C by increasing the heating rates from 1 to 8 °C min\(^{-1}\), respectively. Conversely, the time needed for the thermal decomposition was dramatically decreased with increasing the heating rates. For instance, 7.7 and 1.1 h is needed for the complete combustion of DMP at heating rates of 1 and 8 °C min\(^{-1}\), respectively (Table 1). In addition, the peak height increased approximately ten times with increasing the heating rate from 1 to 8 °C min\(^{-1}\), while the peak maximum
was shifted toward a higher decomposition temperature by 197 °C.

Figure 8 shows the heat released (J g$^{-1}$) during the reaction progress versus the temperature for the DMP where the colored and dashed black curves show the practical and theoretical calculations by AKTS software, respectively. Clearly, there is a perfect match between the experimental and modeled data. The reaction rate (W g$^{-1}$) versus temperature curves showed a good match only at low heating rates (1, 2, and 4 °C min$^{-1}$) which may be due to the large amounts of heat liberated at a high heating rate (8 °C min$^{-1}$) as seen in Figure 9. It is difficult for a good match at high heating rates, and this finding is in line with the work done by Kumar et al. 60

3.2.3. Kinetic Models Discussion. Miscanthus is a lignocellulosic biomass with a composition of cellulose, hemicellulose, and lignin. The first two components decompose in the range of 200–380 °C, while the third component decomposes over a wide temperature range (180–600 °C) and is considered as the rate-determining step during the combustion/pyrolysis of lignocellulosic biomass. 61 Therefore, the model-fitting method is not feasible for detecting the kinetic parameters for DMP as the reaction mechanism is complicated and there are overlapping reactions during the combustion/pyrolysis process. Usually, the TGA analysis shows the thermal decomposition of biomass in three stages of weight loss, namely, dehydration, devolatilisation (active pyrolysis), and char oxidation (passive pyrolysis). 62 The apparent activation energy ($E_a = 22.3$ kJ mol$^{-1}$) calculated with the ASTM-E698 method based on eq 6 is shown in Figure 10. One value of $E_a$ is insufficient to describe the thermal decomposition of DMP as the reaction is complex; hence, the ASTM-E698 method is inaccurate in this case.

The iso-conversional method (model-free) is a convenient method for detecting the kinetic parameters as it provides a variation trend of the $E_a$ and $k_0$ as a function of the reaction progress ($\alpha$). 51 The Flynn-Wall and Ozawa method is more accurate as it shows that the kinetic parameters including the $E_a$ change during the reaction progress. The $E_a$ and the pre-exponential factor ($k_0$) calculated with the FWO method are shown in Figure 10b,c. The variation in the $E_a$ during the reaction progress was in the range of 40–150 kJ mol$^{-1}$. Then, the differential iso-conversional method was used to calculate the kinetic parameters using the AKTS software as in Figures 11 and 12. Figure 11 shows the natural logarithm of the reaction rate (s$^{-1}$) versus the inverse temperature, while the detected $E_a$ along with the $k_0$ are shown in Figure 12 (top curve). From the differential iso-conversional method, the $E_a$ is initially high (at ∼110 kJ mol$^{-1}$) at the start of the reaction where reaction progress was still zero ($\alpha = 0$) while ln($A(\alpha)$ f($\alpha$)) is about 15 s$^{-1}$. It is well-known that the carbohydrate polymers (cellulose and hemicellulose) are tightly bound to the lignin, so it is not
surprising that the \(E_a\) value was high at the start of the reaction as energy is needed to overcome these strong bonds in order for the combustion reaction to proceed. Then \(E_a\) value declined to 40 kJ mol\(^{-1}\) as the \(\alpha\) reached 0.4. Due to the lignocellulosic biomass composition, the mechanism of miscanthus combustion is extremely complex. Cellulose and hemicellulose components decompose in the range of 200–380 °C, while the lignin decomposes over a wide range of temperatures (180–600 °C), and each of these components can combust via parallel exothermic reactions (as shown in the nine-step mechanism). As such, the activation energy should decrease.\(^{61}\)

Finally, as \(\alpha = 0.77\), there was a further increase in the \(E_a\) (>160 kJ mol\(^{-1}\)) which is generally attributed to complex and/or autocatalytic reactions with several steps with the decomposition of lignin and formation of ash.\(^{57}\)

Figure 8. Reaction progress with heat released (J g\(^{-1}\)) versus the temperature for the DMP where the colored and dashed black curves show the practical and theoretical calculations, respectively.

Figure 9. Reaction rate in W g\(^{-1}\) versus the temperature for the DMP where the colored and dashed black curves show the practical and theoretical calculations, respectively.

Table 1. Thermal Decomposition Data of DMP Derived from the DSC Curves at Different Heating Rates\(^{a}\)

| heating rate (°C min\(^{-1}\)) | temperature range (°C) | time range(s) | peak maximum (°C s\(^{-1}\)) | peak height (W g\(^{-1}\)) | heat released (J g\(^{-1}\)) |
|-------------------------------|------------------------|--------------|-----------------------------|--------------------------|--------------------------|
| 1                             | 172–487                | 8822–27722   | 281/1.5 \times 10^4         | 0.794                    | 6260                     |
| 2                             | 180–513                | 4668–14656   | 438/12 \times 10^4          | 1.628                    | 6481                     |
| 4                             | 189–546                | 2464–7822    | 456/6462                    | 3.618                    | 6456                     |
| 8                             | 199–570                | 1302–4088    | 478/3396                    | 7.319                    | 6545                     |

\(^{a}\)Sample weight was \(\approx\)4.9 mg with tangential sigmoid baseline type used during the extraction of DSC data.

Figure 10. Kinetic parameters calculated by different methods: (a) \(E_a\) using the ASTM-E698 method and (b) \(E_a\) and (c) pre-exponential factor using the Flynn-Wall and Ozawa (FWO) method.

Figure 11. Natural logarithm of the reaction rate (s\(^{-1}\)) versus the inverse temperature using the differential iso-conversional method.

Herein, the calculated \(E_a\) using the differential iso-conversional method was in the range of 40–165 kJ mol\(^{-1}\) and in agreement with other studies. Jayaraman et al.\(^{18}\) reported
activation energy values for poplar wood, hazelnut shell, and wheat bran in the range of 66.80\textasciitilde68.56, 83.73\textasciitilde93.25, and 162.17\textasciitilde167.4 kJ mol\(^{-1}\), respectively. Kok and Ozgur reported a variation in the activation energy values between 83.8 and 191.7 kJ mol\(^{-1}\) for hazelnut shell using FWO and KAS methods, respectively.\(^{21}\) Munir et al.\(^{52}\) reported the activation energy for different lignocellulosic biomass such as cotton stalk, shea meal, and sugar cane while the activation energy values ranged from 108 to 116 kJ mol\(^{-1}\). The activation energy was previously reported by Cortes and Bridgwater\(^{44}\) and was in the range of 129\textasciitilde156 kJ mol\(^{-1}\).

3.2.4. Kinetic Models Prediction. The kinetic prediction of DMP isothermal combustion using the AKTS software is shown in Figure 12. Clearly, a temperature higher than 240 °C is needed to start the decomposition of the DMP sample. There was only 10% (\(\alpha = 0.1\)) of the sample decomposed after 1 h at 260 °C. When the temperature was increased to 400 °C, 80% (\(\alpha = 0.8\)) of the DMP decomposed over the same period of time under isothermal conditions. At 480 °C, the DMP sample decomposed completely (\(\alpha = 1\)) after 17.5 min.

3.2.5. Thermal Analysis of Miscanthus Biochar. The thermal pyrolysis of miscanthus biochar-650 (pyrolyzed at 650 °C under \(\text{N}_2\) atmosphere with the TGA and DTG analyses shown in Figure 13a,b). Typically, the active pyrolysis zone (the highest rate of weight loss at rapid thermal decomposition) for any lignocellulosic biomass takes place in the temperature range of 360\textasciitilde490 °C.\(^{33,64}\) However, in the case of DMP, the active zone was at 301 °C with a heating rate of 2.5 °C min\(^{-1}\) and shifted toward higher temperature (333 °C) with a heating rate of 30 °C min\(^{-1}\) (not shown), due to the high content of volatile organics in DMP. During the pyrolysis process, some of these volatile organic compounds are released, and consequently, the active zone of the biochar-650 started at 367 °C at a heating rate of 2.5 °C min\(^{-1}\) with overlapping of a second sharp peak at 405 °C as seen in Figure 13. As expected, the active zone was shifted to a higher temperature and it became broader in the temperature range of 350\textasciitilde600 °C. The biochar yield was calculated according to eq 10.

\[
\text{(% Yield)} = \frac{X}{Y} \times 100
\]

where X and Y are the weights of the produced biochar-650 and the DMP used for the pyrolysis, respectively, where the yield was 40%; this is in agreement with the previous work done by Maiti et al.\(^{63}\) The DSC curve of miscanthus biochar-650 combustion is shown in Figure 13c. There are two clear decomposition peaks around 350 and 400 °C at slow heating rates (i.e., 1, 2, and 4 °C min\(^{-1}\)), while at 8 °C min\(^{-1}\) these two peaks are merged in one broad peak. The miscanthus biochar-650 was easier to combust compared with the DMP as the ignition temperature declined from 295 °C for DMP to 242 °C with a heating rate of 2 °C min\(^{-1}\), as seen in Figure S2. The burnout temperature in contrast increased by about 30 °C for the miscanthus biochar-650. The values of the heat released during the combustion of DMP and miscanthus biochar-650 are comparable at approximately 290 W g\(^{-1}\). The pH of the DMP and the miscanthus biochar-650 solutions were investigated in order to differentiate between the nature of
these two species by soaking and boiling them in deionized water and measuring the pH value prior and after the test using an electronic pH meter (Jenway 3510), as seen in Figure S3. The DMP solution is acidic with a pH of 6.44 due to the leaching of the acidic organic groups of cellulose, hemicellulose, and lignin. On the other hand, miscanthus biochar-650 solution is basic with pH of 9.79 due to the leaching of the alkali metal salts in the biochar. These results were also supported by the SEM analysis using the backscattered electron detector (BSED) at a magnification of 1000x.

4.1. Miscanthus Ash in Fertilizer Composition. The XRD pattern of miscanthus ash in Figure S4 shows the presence of various inorganic potassium salts such as potassium hydrogen disilicate (KHSi2O5) and potassium chloride (KCl) which are the most dominant constituents in the miscanthus ash, along with K2H2(CO3)·11/2 H2O and KHCO3. These inorganic salts represent 23.8 wt% of the miscanthus ash, as seen in Figure S5. These results were also supported by the SEM analysis using the backscattered electron detector (BSED) and in agreement with the literature for woody ash. Lighter spots are apparent in the miscanthus ash SEM which also indicate the presence of these inorganic salts, as seen in Figure 14, the inference being that miscanthus ash can be used as a potential source of potassium in the fertilizer industry.

4.2. Application of Dry Miscanthus Plant and Its Biochar in Heavy Metal Removal. We selected Cd for the heavy metal removal test as like other heavy metals it is extremely dangerous even at very low concentrations. It is obvious that both biochar-650 and biochar-950 are more active than DMP in Cd removal, most likely due to the formation of activated carbon in the biochar. High percentage removals capacities of 93, 99.4, and 99.9% for DMP, biochar-650, and biochar-950, respectively, over 7 days were detected as seen in Figure 15. Most of the percent removal was achieved in the first hours of the test, making the DMP or its biochar derivatives potentially ideal in the continuous treatment of wastewater or other polluted waste streams. There is the requirement for future research to examine what miscanthus pretreatments might improve its efficiency in removing heavy metals from aqueous solutions followed by additional downstream recovery.

5. CONCLUSIONS

Herein, the thermal and kinetic analyses of dry miscanthus plant and its char were investigated. The activation energy was calculated using the ASTM-E698 method and was determined to be 22.3 kJ mol⁻¹. One value of Eₚ, however, is insufficient to describe the thermal decomposition of lignocellulosic biomass (miscanthus) as the reaction is complex; hence, the ASTM-E698 method was inaccurate. The Eₚ and the pre-exponential factor (kₒ) were therefore calculated with the FWO method, which showed a variation in the Eₚ during the reaction progress in the range of 40–150 kJ mol⁻¹. The differential iso-conversional method showed activation energy values in the range of 40–165 kJ mol⁻¹. Therefore, the FWO and differential iso-conversional methods were more accurate than the ASTM-E698 method for calculating the activation energy and the kinetic parameters during the combustion/pyrolysis process of the DMP. The kinetic prediction of DMP isothermal combustion showed that a temperature higher than 240 °C is needed to start decomposition of the DMP sample. The miscanthus biochar-650 was found to be promising in terms of its enhanced combustibility. There is the potential for a new application of miscanthus in wastewater treatment; in particular, the fast removal of heavy metals such as cadmium. Moreover, miscanthus ash could potentially be used as a source of potassium in the fertilizer industry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b03478. Images of miscanthus, DSC curves, pH of the DMP and miscanthus biochar-650, XRD pattern, EDX data, and elemental and proximate analysis (PDF)

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