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Pyrolytic characteristics and kinetic studies of agricultural wastes—Four kinds of grasses

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ABSTRACT
Several grasses are among the agricultural wastes generated annually in a large quantity during farming activities. In this study, thermogravimetric analysis was used to evaluate the fuel properties of a number of grasses, including Aeluropus sinensis, Conyza canadensis, Imperata cylindrica, and Setaria viridis. The pyrolysis behavior was also compared with the other biomasses. The thermal reaction systems fitted well with the distributed activation energy model and the global kinetic model and it is obvious that the values of $E$ and $k_0$ calculated by the distributed activation energy model were much higher than that of the global kinetic model.

KEYWORDS
Agricultural wastes; distributed activation energy model; grasses; kinetic analysis; pyrolytic characteristics

Introduction
Biomass is one of the most promising renewable energy sources because of its versatile application potential. Several grasses, such as Aeluropus sinensis, Conyza canadensis, Imperata cylindrica, and Setaria viridis, are among the agricultural wastes generated annually in a large quantity during farming activities. They can adapt to several stressful environmental conditions, including high saline content, drought, and heavy metal pollution, and can even develop new ecotypes to survive in extreme environments. However, the negative impacts of them on agriculture include severe crop losses and high investment in labor for weeding (Bello and Banjo, 2012). Farmers prefer to clear these grasses by burning them off, which leads to loss in soil fertility and environmental pollution.

Pyrolysis has drawn much attention owing to its ability to acquire fuel and valuable chemicals from biomass. The pyrolysis process on a large variety of biomasses has been extensively studied (Otero et al., 2008; Cai and Bi, 2009; Ion et al., 2013). Thermogravimetric studies showed that each kind of biomass had unique pyrolysis characteristics, by virtue of the specific proportions of the components present in it (Lira et al., 2010). Although the thermal decomposition reactions have been studied for many years, the best reaction model and kinetic parameters for the thermal decomposition of different types of biomasses are still discussed by the scientific community (Santos et al., 2012). Furthermore, there is less information describing the fuel properties of Aeluropus sinensis, Conyza canadensis, Imperata cylindrica, and Setaria viridis, and there have been few studies comparing the energetic properties of them to other biomasses. The present study has evaluated the fuel properties of a number of grasses including Aeluropus sinensis, Conyza canadensis, Imperata cylindrica, and Setaria viridis. The pyrolysis behavior was analyzed and compared with that of other biomasses. Finally, the kinetic parameters were determined by both the distributed activation energy model (DAEM) and the global kinetic model.

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Materials and methods

Materials

Four kinds of grasses were collected from the agricultural field of Yantai, Shandong province, China. The grasses were oven-dried at 60°C to a constant dry weight, and then grounded with a Mini-Mill to pass through a 125-μm sieve.

Proximate, ultimate, and thermogravimetric analysis

The proximate, ultimate, and thermogravimetric analysis were carried out according to a previous study (Li et al., 2013). The temperature of the furnace was programmed to rise from room temperature to 900°C.

Kinetic analysis using DAEM

DAEM assumes that many irreversible first-order parallel reactions that have different rate parameters occur simultaneously. The model is expressed as the following equation:

$$\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{k_0 R}{E} \right) + 0.6075 - \frac{E}{RT}.$$  \(1\)

Equation (1) establishes a linear relationship between \(\ln(\beta/T^2)\) and \((1/T)\) with the slope of \((-E/R)\), where \(\beta\) is the heating rate and \(R\) is the universal gas constant. Activation energy \(E\) and frequency factor \(k_0\) can be determined by the slope and intercept of the Arrhenius plots.

Kinetic analysis using the global kinetic model

The global kinetic model for presenting thermal decomposition of biomass is categorized as the separate-stage model, and the pyrolytic reactions under inert atmospheres are assumed to be governed by first-order Arrhenius law. With regard to the notable mass loss stage, the global kinetic model is described by (Di Blasi, 1998; Grieco and Baldi, 2011; Shen et al., 2011):

$$\ln \left[ \frac{\ln(1-\alpha)}{T^2} \right] = \ln(\frac{k_0 R}{E}) - \frac{E}{RT},$$  \(2\)

where \(\alpha = (m_0 - m_t)/(m_0 - m_\infty)\), \(m_t\) is the mass loss by time \(t\), \(m_0\) is the mass loss at the end of pyrolysis, and \(m_\infty\) is the mass loss at the end of pyrolysis. The values of \(E\) and \(k_0\) can be determined by the slope and intercept of the Arrhenius plots.

Results and discussion

Proximate and ultimate analysis

The ash content of four grass species falls in the range of 2.6–12.7 wt% (Table 1). Conyza canadensis is lower in ash content than the other grasses and Setaria viridis is characterized by the highest ash content. Ultimate analysis shows that grasses consists of moderately high carbon content and low amounts of nitrogen, hydrogen, and sulfur (Table 1), and the carbon, hydrogen, and nitrogen contents are similar to woods, such as birch (Shen et al., 2009).
Pyrolysis behavior

The heating rate is one of the most important parameters influencing the thermal decomposition of grasses. There was a shift in the maximum decomposition rate and the temperature corresponding to the peak decomposition rate increased (Figure 1 and Table 2). This is due to the effect that the time to reach a given temperature becomes shorter by an increased heating rate. Therefore, more time has...
to elapse before the reaction is complete, which causes the entire curve to shift to higher temperatures.

Characteristics of the thermal degradation for the four grass species at different heating rates are shown in Table 2. Mass loss rate is an indication of the reactivity of the biomass under investigation. The average mass loss rate at the heating rate of 10°C min\(^{-1}\) was 0.0125, 0.0125, 0.0126, and 0.0115% s\(^{-1}\) for *Aeluropus sinensis*, *Conyza canadensis*, *Imperata cylindrica*, and *Setaria viridis*, respectively (Table 2), which indicated that *Setaria viridis* has a little higher pyrolysis reactivity under a nitrogen atmosphere.

According to the decomposition of the mixture of pure hemicelluloses, cellulose, and lignin (Mui et al., 2008) at the heating rate of 5°C min\(^{-1}\), it is indicated that the major degradation of the first step, which occurred between 170 and 299°C, 172 and 293°C, and 182 and 304°C for *Aeluropus sinensis*, *Imperata cylindrica*, and *Setaria viridis*, respectively, was mainly hemicellulose but lignin is also involved to a small extent, because it undergoes slow decomposition over a wide temperature range. The second step occurred between 299 and 384°C, 293 and 237°C, and 304 and 382°C for *Aeluropus sinensis*, *Imperata cylindrica*, and *Setaria viridis*, respectively. This was due to mostly cellulose decomposition whereas lignin continued its rather slow degradation. This result was in good agreement with the study of Sonobe and Worasuwannarak (2008), who reported that cellulose decomposes between 300 and 390°C at the heating rate of 5°C min\(^{-1}\). After the major degradation is completed, it is believed that the long tailing section represents constant decomposition of pyrolysis residue and lignin distributed along a wide range of temperature intervals (Vamvuka et al., 2003; Munir et al., 2009).

### Table 2. Characteristics of the thermal degradation for *Aeluropus sinensis*, *Conyza canadensis*, *Imperata cylindrica*, and *Setaria viridis* at different heating rates.

| Species           | Heating Rate, °C min\(^{-1}\) | \(T_i\), °C | \(T_f\), °C | \(T_1\), °C | \(T_2\), °C | \((-\alpha/dt)_{\text{average}}\), % s\(^{-1}\) | \((-\alpha/dt)_{\text{max}}\), % s\(^{-1}\) | Mass Loss, % |
|-------------------|-------------------------------|----------|---------|---------|---------|--------------------------|--------------------------|-----------|
| *Aeluropus sinensis* | 5                             | 162      | 384     | 272     | 334     | 0.0062                   | 0.0566                   | 65.00     |
|                   | 10                            | 170      | 399     | 289     | 354     | 0.0125                   | 0.1053                   | 65.73     |
|                   | 20                            | 184      | 405     | 297     | 359     | 0.0250                   | 0.1935                   | 65.86     |
|                   | 30                            | 200      | 405     | 297     | 359     | 0.0370                   | 0.2851                   | 65.07     |
| *Conyza canadensis* | 5                             | 141      | 373     | 313     | 353     | 0.0066                   | 0.0667                   | 69.73     |
|                   | 10                            | 151      | 376     | 325     | 365     | 0.0125                   | 0.1299                   | 65.91     |
|                   | 20                            | 170      | 387     | 335     | 365     | 0.0252                   | 0.2459                   | 66.20     |
|                   | 30                            | 181      | 402     | 341     | 361     | 0.0365                   | 0.3577                   | 63.94     |
| *Imperata cylindrica* | 5                             | 160      | 409     | 262     | 331     | 0.0062                   | 0.0591                   | 64.78     |
|                   | 10                            | 172      | 424     | 268     | 341     | 0.0126                   | 0.1115                   | 66.28     |
|                   | 20                            | 182      | 429     | 280     | 351     | 0.0241                   | 0.2075                   | 63.24     |
|                   | 30                            | 206      | 438     | 285     | 358     | 0.0357                   | 0.3024                   | 62.57     |
| *Setaria viridis* | 5                             | 169      | 382     | 282     | 336     | 0.0059                   | 0.0557                   | 62.13     |
|                   | 10                            | 182      | 394     | 291     | 347     | 0.0115                   | 0.1099                   | 60.55     |
|                   | 20                            | 192      | 400     | 300     | 357     | 0.0230                   | 0.1998                   | 60.36     |
|                   | 30                            | 203      | 423     | 307     | 363     | 0.0335                   | 0.2923                   | 58.79     |

\(^aT_i\) is the initial temperature of the major mass loss stage.

\(^bT_f\) is the final temperature of the major mass loss stage.

\(^cT_1\) is the temperature corresponding to the smaller peak of the DTG curve.

\(^dT_2\) is the temperature corresponding to the larger peak of the DTG curve.

### DAEM analysis

The kinetic analysis included the recording of mass loss curves at different heating rates in order to deduce the dependence of kinetic parameters on the conversion level. The linear development for different conversion rates from 0.10 to 0.90 at various heating rates are shown in Table 3. It exhibited high linear correlation coefficients (>0.97), indicating that the thermal decomposition of the four samples under inert atmosphere probably undergoes a set of first-order reactions. The average activation energies were 172.37, 179.77, 213.89, and 186.18 kJ mol\(^{-1}\) for *Aeluropus sinensis*, *Conyza canadensis*, *Imperata cylindrica*, and *Setaria viridis*, respectively (Table 3).
The activation energies of *Aeluropus sinensis, Conyza canadensis, Imperata cylindrical*, and *Setaria viridis* were widely distributed so that each conversion rate had individually corresponding activation energy during the pyrolysis processes (Figure 2). The relationship of the conversion rate and the activation energies suggested that the activation energies varied with the parabolic shapes during the pyrolysis processes for *Imperata cylindrica* and *Setaria viridis*, which exhibited a single peak at the conversion rate of 0.48. Previous research indicated that this ‘jump’ may be due to the overlap between

![Figure 2. Relationship between conversion rate and activation energy for Aeluropus sinensis (●), Conyza canadensis (○), Imperata cylindrica (▲), and Setaria viridis (△).](image)

**Table 3.** Kinetic parameters analyzed by DAEM for *Setaria viridis, Conyza canadensis, Imperata cylindrical, and Aeluropus sinensis.*

| Conversion Rate | $E$, kJ mol$^{-1}$ | $k_0$, s$^{-1}$ | $R^2$ | $E$, kJ mol$^{-1}$ | $k_0$, s$^{-1}$ | $R^2$ |
|----------------|------------------|----------------|------|------------------|----------------|------|
| 0.1            | 180.23           | $3.63 \times 10^{12}$ | 1.00 | 187.25           | $6.23 \times 10^{13}$ | 1.00 |
| 0.2            | 178.43           | $7.56 \times 10^{11}$ | 1.00 | 185.91           | $7.18 \times 10^{12}$ | 1.00 |
| 0.3            | 177.46           | $2.43 \times 10^{11}$ | 0.99 | 179.87           | $5.03 \times 10^{11}$ | 1.00 |
| 0.4            | 175.76           | $6.72 \times 10^{10}$ | 0.98 | 180.75           | $2.27 \times 10^{11}$ | 1.00 |
| 0.5            | 172.60           | $1.33 \times 10^{10}$ | 0.97 | 178.71           | $6.88 \times 10^{10}$ | 1.00 |
| 0.6            | 173.90           | $7.54 \times 10^{9}$  | 0.97 | 178.56           | $3.78 \times 10^{9}$  | 1.00 |
| 0.7            | 173.49           | $3.71 \times 10^{9}$  | 0.98 | 175.31           | $1.19 \times 10^{9}$  | 1.00 |
| 0.8            | 168.19           | $7.87 \times 10^{8}$  | 0.98 | 174.36           | $6.27 \times 10^{8}$  | 1.00 |
| 0.9            | 151.27           | $1.67 \times 10^{7}$  | 0.97 | 177.20           | $6.02 \times 10^{7}$  | 1.00 |
| Average        | 172.37           |                  |      | 179.77           |                  |      |

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hemi-/cellulose and lignin (Wongsiriamnuay and Tippayawong, 2010). Additionally, the \( E \) values from *Aeluropus sinensis*, *Conyza canadensis*, and *Setaria viridis* changed slightly in the major mass loss process, whereas the \( E \) values of *Imperata cylindrical* varied greatly from 176.27 to 235.89 kJ mol\(^{-1}\).

It can be seen that the values of the frequency factor \( k_0 \) changed greatly with different \( E \) values (Table 3). *Aeluropus sinensis*, for example, demonstrates that the \( k_0 \) values increased from an order of 10\(^7\) to an order of 10\(^12\) s\(^{-1}\), whereas the \( E \) values increased from 151 to 180 kJ mol\(^{-1}\). This suggests a compensation for the decrease of the reaction rate constant caused by increasing activation energy. This relationship is known as the compensation effect (Lakshmanan et al., 1991).

### Global kinetic analysis

The global kinetic parameters of *Aeluropus sinensis*, *Conyza canadensis*, *Imperata cylindrical*, and *Setaria viridis* at different heating rates are shown in Table 4, together with the temperature region corresponding to the main mass loss stage. It was found that the activation energies for grasses under nitrogen atmosphere varied in a narrow range as the heating rate increased, resulting in a high correlation coefficient (>0.98). It is obvious that the values of \( E \) and \( k_0 \) calculated by the DAEM were much higher than that derived from the global kinetic model (Tables 3 and 4). It is also obvious that DAEM can represent the intrinsic pyrolysis mechanism of *Aeluropus sinensis*, *Conyza canadensis*, *Imperata cylindrical*, and *Setaria viridis* better than the global kinetic model.

### Conclusions

Thermogravimetric analysis was used to evaluate the fuel properties of a number of grasses, including *Aeluropus sinensis*, *Conyza canadensis*, *Imperata cylindrica*, and *Setaria viridis*. Thermogravimetry and derivative thermogravimetry curves shifted towards higher temperature ranges when the heating rate increased. The major mass loss started at 151, 170, 172, and 182°C at the heating rate of 10°C min\(^{-1}\) for *Conyza canadensis*, *Aeluropus sinensis*, *Imperata cylindrica*, and *Setaria viridis*, respectively. The pyrolysis behavior was also compared with the other biomasses. The distributed average activation energies of the four grass species fall in 172–214 kJ mol\(^{-1}\) and the frequency factor \( k_0 \) changed greatly with different \( E \) values. The results exhibited that the values of \( E \) and \( k_0 \) calculated by the DAEM were much higher than that derived from the global kinetic model. The thermal reaction systems fitted well with the DAEM and the global kinetic model.

Table 4. Global kinetic parameters for *Aeluropus littoralis*, *Conyza canadensis*, *Imperata cylindrical*, and *Setaria viridis*.

| Biomass     | Heating Rate, °C min\(^{-1}\) | Temperature Range, °C | \( E \), kJ mol\(^{-1}\) | \( k_0 \), s\(^{-1}\) | \( R^2 \) |
|-------------|-------------------------------|------------------------|---------------------------|-------------------------|--------|
| *Aeluropus* | 5                             | 162–384                | 73.89                     | 8.22                    | 0.98   |
|             | 10                            | 170–389                | 70.32                     | 5.02                    | 0.98   |
|             | 20                            | 184–399                | 70.06                     | 7.45                    | 0.98   |
|             | 30                            | 200–405                | 71.54                     | 13.10                   | 0.98   |
| *Conyza*    | 5                             | 141–373                | 72.36                     | 7.25                    | 0.99   |
| *canadensis*| 10                            | 151–367                | 73.27                     | 13.99                   | 0.99   |
|             | 20                            | 170–387                | 71.32                     | 13.00                   | 0.99   |
|             | 30                            | 181–402                | 71.09                     | 15.22                   | 0.99   |
| *Imperata*  | 5                             | 160–409                | 62.85                     | 0.60                    | 0.99   |
| *cylindrica*| 10                            | 172–424                | 60.48                     | 0.57                    | 0.99   |
|             | 20                            | 182–429                | 62.77                     | 1.53                    | 0.99   |
|             | 30                            | 206–438                | 63.73                     | 2.43                    | 0.99   |
| *Setaria*   | 5                             | 169–382                | 78.39                     | 17.24                   | 0.99   |
| *viridis*   | 10                            | 182–394                | 78.33                     | 24.93                   | 0.99   |
|             | 20                            | 192–400                | 78.62                     | 40.00                   | 0.99   |
|             | 30                            | 202–423                | 78.24                     | 44.44                   | 0.99   |
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