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Thermogravimetric characterization of corn stover as gasification and pyrolysis feedstock

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ABSTRACT

Interest in generating energy from biomass has grown tremendously in recent years. Corn stover is an agricultural by-product, which is abundant in quantity. Gasification and pyrolysis are efficient methods of harnessing energy efficiently from corn stover. The performances of mathematical models to predict the product gas quality rely on characterization of feed materials and the reaction kinetics of their thermal degradation. The objective of this research was to determine selected physical and chemical properties of corn stover related to thermochemical conversion. Thermogravimetric analyses were performed at heating rates of 10, 30, and 50 °C min^{-1} in nitrogen (inert) and air (oxidizing) atmospheres. The parameters of the reaction kinetics were obtained and compared with other biomass. The weight losses of corn stover in both inert and oxidizing atmospheres were found to occur in three stages.

1. Introduction

Plants convert solar energy into chemical energy and store it in the form of structural components of biomass using the CO_2 in the atmosphere. Harnessing energy from biomass is environmental friendly as it does not contribute to an increase in CO_2 in the atmosphere [1]. Interest in energy from biomass, or so-called bioenergy, also has been enhanced because biomass can be generated locally and can make any country energy self-sustainable and less dependent on foreign petroleum resources.

Corn is the most widely planted crop in the United States, which makes corn stover very abundantly available, especially in the mid-western region of the United States. Corn stover production, nationwide, is estimated to be 204 Mt year^{-1} (dry basis). Assuming that 40% of the corn stover produced can be harvested on a sustainable basis, 82 Mt year^{-1} (dry basis) are available. The estimated availability of the next most available agricultural residue, wheat straw, is estimated to be around 30 Mt year^{-1} (dry basis) [2]. The large amount of available corn stover makes it an ideal candidate as the future feedstock for bioenergy production.

Within the last few decades, the conversion of starch to ethanol has been made economical and production of ethanol from starch has grown tremendously. However, the total potential of ethanol production from starch-based feedstock is only a small part of total fuel consumption demand in US. Another category of biomass is lignocellulosic feedstock, which has the potential to meet a large part of the current energy demand and is comparatively cheaper than the starch-based feedstocks. Conversion of lignocellulosic material to ethanol is facing many challenges; among them are the separation of cellulose and hemicellulose from the lignocellulosic material (delignification), and conversion of

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cellulose and hemicellulose to fermentable sugars and then to ethanol via fermentation. The process of making this economical is still being studied [3].

Gasification is a thermochemical process by which any carbonaceous feed can be converted to gaseous products with useable heating value (primarily carbon monoxide and hydrogen in a controlled oxidizing atmosphere). Pyrolysis is a sub-category of gasification, the difference being this process takes place in an inert atmosphere (generally nitrogen) [4].

Gasification and pyrolysis can convert lignocellulosic materials to synthesis gas (syngas) without the need for delignification. Synthesis gas can be further converted to other chemicals (by various reforming processes) or fuels (by the Fischer–Tropsch method) or hydrogen can be separated for fuel cell application. As compared to combustion, gasification can utilize the feedstock efficiently producing a variety of compounds for replacing petrochemical-derived products. One more advantage of gasification, as compared with other bioenergy generation techniques, is its ability to utilize a wide range of feedstocks ranging from any plant residue, organic by-product (with protein, lignin or oil) of industry or even municipal wastes. So, gasification and pyrolysis are considered viable options for processing biomass feedstocks, which cannot be fermented to ethanol technically or economically.

Mathematical modeling to predict the product gas qualities during gasification and pyrolysis requires the knowledge of reaction kinetics of the volatilization of biomass and subsequent reactions. Thermogravimetric analysis (TGA) is very useful in determining the reaction kinetics of gasification and pyrolysis. It has been used extensively for the characterization of various feedstocks. Researchers have used this method to determine the kinetics parameter for rice husk in an oxygen atmosphere [5], bagasse in a nitrogen atmosphere [6,7], forestry wastes in a nitrogen atmosphere [8] and rapeseed straw and stalks in a nitrogen atmosphere [9]. However, there is a lack of kinetics information on gasification or pyrolysis of corn stover. The objectives of this project were to obtain properties of corn stover related to thermochemical conversions, and to determine and analyze the reaction kinetics of corn stover in inert and oxidizing atmospheres using a thermogravimetric technique.

2. Material and methods

2.1. Biomass sample preparation

Corn (*Zea mays*) stover without any corn cob was collected from the University of Nebraska Roger's farm near Lincoln, NE, soon after grain harvesting at maturity in October 2006. The stover was ground with a Thomas Wiley Mini-Mill (Thomas Scientific, Swedesboro, NJ) to pass through a #20 sieve.

2.2. Physical property measurements

The moisture contents of the samples were measured using a Halogen moisture analyzer (Mettler-Toledo Inc., Columbus, OH). ASABE Standard S319.3 was used to determine the size distribution of the ground samples (ASABE standards, 2006).

2.3. Energy content

The energy contents of the samples were measured using an adiabatic oxygen bomb calorimeter (Model: 1241, Parr Instrument, Moline, IL). The energy content of the dry matter was then calculated. The ground samples were first put into gelatin capsules for combustion in the calorimeter but it was observed that all of the samples did not combust completely. So, the ground samples were pelletized into short cylinders 3.92 mm long with tapered edges with a maximum diameter of 15.6 mm. In this way, the ground sample was compacted from an original average density of 180 to 1181 kg m^{-3}. The pellet was then combusted to determine energy content.

2.4. Ultimate analysis

Elemental compositions of the samples were measured by Midwest Microlab, LLC (Indianapolis, IN, USA). Carbon, hydrogen and nitrogen compositions were performed by combustion at 990 °C using the elemental analyzer. Oxygen was determined gravimetrically by pyrolysis at 1200 °C. Sulfur was determined via flask combustion and subsequent titration.

2.5. TGA experiments

TGA experiments were performed using TGA (Perkin-Elmer TGA 7, Norwalk, CT). Temperature, furnace and weight of the TGA were calibrated according to the manufacturer's recommendation. Temperature calibration was performed by measuring Curie points of alumel, nickel, perkalloy and iron. The kinetics of weight loss at a heating rate of 5 °C min^{-1} for Avicel PH 105 cellulose (FMC Corp, Newark, DE, USA) was cross-checked with data reported by Grönli et al. [10]. The activation energy (E) and logarithm of pre-exponetial factor ($\log A$) for first-order reaction were found to be 241 kJ mol^{-1} and 20.0 s^{-1}, respectively, which were very close to the reported values by Grönli et al. [10].

Approximately 5–10 mg of the corn stover samples was placed in the pan of the TGA microbalance, which was enough to fill the pan because of the low density of the ground corn stover. Nitrogen gas and air were used as purge gases. All TGA experiments were conducted at a constant purge flow rate of 40 mL min^{-1}. Residual weight of the sample and the derivative of weight, with respect to time and temperature (differential thermogravimetry analysis, DTG), were recorded using TGA7 software.

Experiments were conducted at temperature scan rates (heating rates) of 10, 30 and 50 °C min^{-1}. Samples were held at 25 °C for 1 min, heated to 850 °C at the respective temperature scan rates and then held at 850 °C for 1 min.

3. Procedure to determine parameters of reaction kinetics

Parameters of the reaction kinetics were determined using the procedure of Duvvuri et al. [11] as applied by Mansaray and Ghaly [5] and Karaosmanoglu et al. [9].

Global kinetics of the vitalization reaction can be written as

$$-\frac{dx}{dt} = kx^n, \tag{1}$$

where x is the sample weight, k the reaction constant and n the order of the reaction.

Applying the Arrhenius equation,

$$k = Ae^{-E/RT}. \tag{2}$$

The combined form of the above two equations (1) and (2) can be written in linear form as

$$\ln\left[\frac{-1}{w_o - w_f}\frac{dw}{dt}\right] = \ln(A) - \left(\frac{E}{RT}\right) + n\ln\left(\frac{w - w_f}{w_o - w_f}\right), \tag{3}$$

where w_o is the initial weight at the start of that stage, w_f the final weight at the end of that stage, w the weight at any time, dw/dt the ratio of change in weight to change in time, A the pre-exponential factor and R the universal gas constant (gas value).

Eq. (3) is of the form

$$y = B + Cx + Dz, \tag{4}$$

where

$$y = \ln\left[\frac{-1}{w_o - w_f}\frac{dw}{dt}\right], \quad x = \frac{1}{T}, \quad z = \ln\left(\frac{w - w_f}{w_o - w_f}\right),$$

$$B = \ln(A), \quad C = \left(-\frac{E}{R}\right), \quad D = n.$$

The constants B, C, D were estimated by multi-linear regression of the TGA data for each stage using Microsoft Excel.

The integral form of Eq. (1) was used to determine the predicted values of the residual weight using the estimated constants. The predicted values were then compared with the experimental residual weight losses.

4. Results and discussion

After grinding the corn stover for all the analyses, the geometric mean diameter or median size of particles was 0.443 mm with a standard deviation of 0.181 mm. The energy content (higher heating value) of the corn stover pellets was 18.45±0.23 MJ kg^{-1}, which was higher than the energy content of pigeon pea stalk [12] and rapeseed straw (17.64 MJ kg^{-1}) [9] but similar to pine chips (18.98 MJ kg^{-1}) [13] and rice husk (14.42–18.31 MJ kg^{-1}) [14].

Tables 1 and 2 summarize the composition of corn stover based on proximate and ultimate analyses [15]. The elemental compositions obtained by other researchers were similar, but the composition of cellulose, hemicellulose and lignin varied from 28% to 51%, 19.1% to 30.7% and 11% to 16.9%, respectively.

4.1. *Nitrogen (inert) atmosphere*

A typical TGA plot of corn stover in a nitrogen atmosphere is shown in Fig. 1. The first stage of weight loss ranged from 25 °C to around 125 °C (Table 3) depending on the heating rate (temperature scan rate), which was clearly distinct from the other stages of weight loss. The derivative plot (DTG) had a separate peak for this zone of weight loss (Fig. 1). As suggested by Mansaray and Ghaly [5], it may correspond to the loss of water and light volatile compounds in the biomass sample. The low moisture content in our corn stover sample resulted in low weight loss during this stage of weight loss.

Following the first stage, there was negligible weight loss ($<$0.5%) in the temperature range of 160–250 °C. The second phase of weight loss started around 250 °C. The derivative plot of the region between 250 and 850 °C showed only one observable peak. When the data between 250 and 850 °C were used for determining parameters of reaction kinetics, the r^2 values for the multiple-regression were less than 0.80, and the predicted values deviated from the experimental data. This suggested that there may have been two different reaction stages of weight loss occurring in this region (250–850 °C). Then, this region was divided into two regions (stages) by the intersection of the tangents from the descending part of the peak and the linear part of the DTG plot. The temperature at the intersection was 420–470 °C depending on the heating rates. Separate reaction kinetics for the temperature ranges of the above resulted in very high r^2 values ($>$0.90). The predicted weight loss matched the actual experimental weight loss very well (Fig. 2).

From the above observations, it was concluded that the total of three distinct stages (Fig. 1) represented the global kinetics of weight loss occurring during TGA of corn stover in inert atmosphere.

4.1.1. *Parameters of reaction kinetics*

The temperature range between 250 and 450 °C resulted in reaction kinetics of order 0.75 (close to first-order reaction) with r^2 values greater than 0.90 (Table 4). The activation energy of the reaction during this stage was approximately 60 kJ mol^{-1}. Weight loss during this stage was rapid, so it was designated as the active pyrolysis zone. As other researchers [22,23] suggested, it may correspond to the major loss (decomposition) of cellulose and hemicellulose components and partial loss of the lignin component of the corn stover. Later, Biagini et al. [24] performed TGA analyses of cellulose, hemicellulose and lignin separately and confirmed that TGA plots showed the loss of hemicellulose started first,

Table 1 – Proximate and ultimate analyses of corn stover

Authors	Kitani and Hall [16]	Demirbas [17]	Evans et al. [18]	Our corn stover sample
Ultimate analysis (wt% dry)				
C	43.7	49.5	46.5	47.4±0.13
H	5.56	5.4	5.81	5.01±0.11
O	43.3	41.8	39.7	38.09±0.25
N	0.61	0.6	0.56	0.77±0.03
S	0.01		0.11	0.31±0.03
Cl	0.6			
Proximate analysis (wt% dry)				
Ash	5.6	3.7	7.3	8.18±0.08
Volatiles	75.2		78.1	74.85±1.40

Table 2 – Summary of biochemical analyses of corn stover [15]

Authors	Lee [19]	Lynd et al. [20]	Richard and Trautman [21]	Demirbas [17]	Evans et al. [18]
Cellulose	39	36.4	28	51.2	36.8
Hemicellulose	19.1	22.6	28	30.7	25.4
Lignin	15.1	16.6	11	14.4	16.9
Total ash+biochemical	81.5	85.3	74	100	86.4

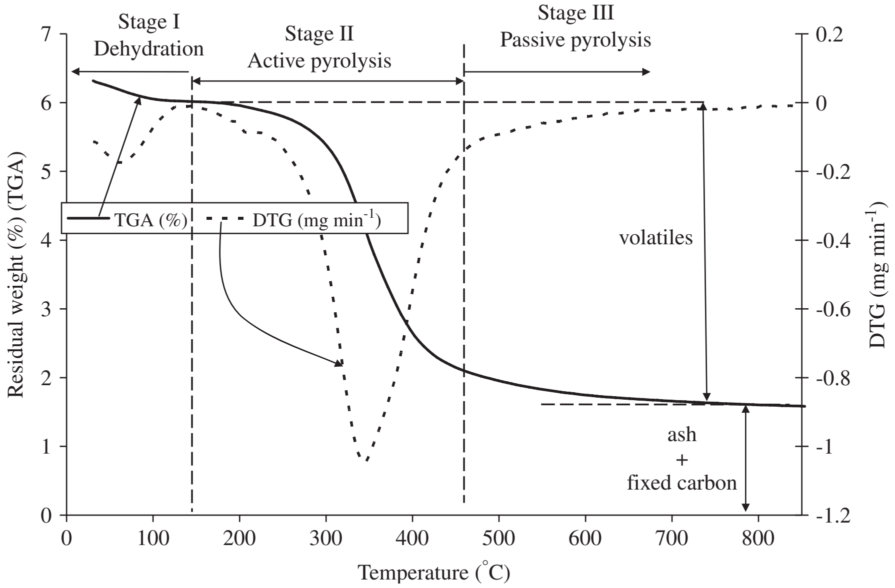

Fig. 1 – Typical TGA diagram of corn stover in a nitrogen atmosphere.

Table 3 – Temperature range and weight loss in a nitrogen atmosphere

	10 °C min^{-1}		30 °C min^{-1}		50 °C min^{-1}	
	Temperature (°C)	Wt (%)	Temperature (°C)	Wt (%)	Temperature (°C)	Wt (%)
Stage I	25	100	25	100	25	100
	110	95.92	135	94.50	140	93.73
Stage II	250	91.06	260	90.23	260	90.38
	420	34.75	435	35.17	470	34.13
Stage III	420	34.75	435	35.17	470	32.56
Ash+fixed carbon	850	24.94	850	24.89	850	24.44

which then overlapped with the loss of cellulose. Loss of lignin was slow and occurred over a wide range of temperature.

Following this stage, there was a continuous and slow weight loss from 420–470 to 850 °C. The order of the reaction was 0.07, which suggested that it was a zero-order reaction. Because of the slow rate of weight loss, this third stage was represented as the passive pyrolysis zone. As discussed earlier, this stage may have been due to the thermal degradation of lignin or complex high-molecular weight components of corn stover.

The TGA plot of corn stover was similar to the TGA plots of rice husk [16] and microalgae [25]. But the temperature ranges of the stages of rice husk were different from those of the corn stover samples.

4.1.2. *Effect of heating rate*

Heating rate (temperature scan rate) had an effect on the temperature range of the stages of the reaction (Fig. 3 and Table 4). Increasing the heating rate appeared to increase the start and end temperatures of each stage, which may have been due to the heat transfer limitations. Also, it should be

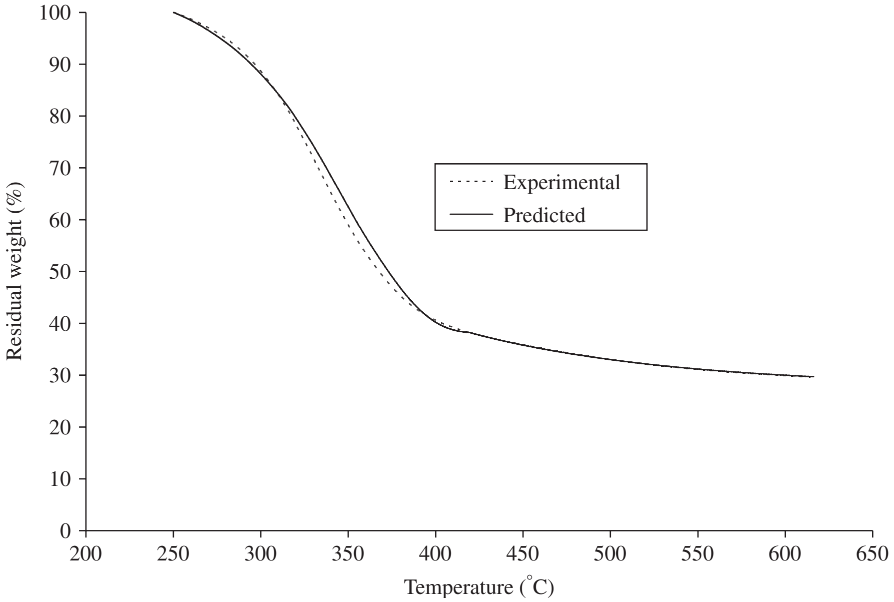

Fig. 2 – Experimental versus predicted weight loss in the temperature range of 250–800 °C, assuming two separate stages of weight loss.

Table 4 – Kinetic parameters during second stage in a nitrogen atmosphere

	A (s^{-1})	E (kJ mol^{-1})	n	r^2
10 °C min^{-1}	1.35×10^4	57.95	0.74	0.91
30 °C min^{-1}	7.33×10^4	62.62	0.76	0.92
50 °C min^{-1}	4.42×10^4	58.94	0.83	0.91

noted that temperatures mentioned herein may not have been the actual sample temperature, but rather the temperatures of the purge gas flowing over the sample near the sample holder (generally typical of thermogravimetric instruments). High heating rates and large mass loading tend to deflect the measured temperature from the actual sample temperature [26]. With an increase in heating rate, a longer time may be required for the purging gas to reach equilibrium with the temperature of the furnace or the sample because of the heat transfer limitations. However, as expected, heating rate did not affect the total weight loss at any stage.

4.2. *Air atmosphere (oxidizing)*

In an air atmosphere, the TGA plots (Fig. 4) clearly suggested that there were three stages of weight loss. The first stage in the oxidizing atmosphere ranged from 25 to 115–140 °C (Table 5). It was very similar to the first stage in the inert atmosphere. The loss of water and volatilization of light molecules may have contributed to weight loss in this stage.

Similar to the inert atmosphere condition, the weight loss between the end of the first stage (130 °C) and the start of the next stage (240 °C) was much less (<5%). The second stage of weight loss ranged from 240 to 350–400 °C. In this region, there was a very large weight loss (~70%) at a very high rate (>10% °C^{-1}) as compared with the amount (~56%) and rate of weight loss (<0.7% °C^{-1}) in the inert atmosphere, which may have been as a result of the oxidation of a substantial part of the corn stover.

Separation between the second and third stages in the oxidizing atmosphere was very clear. The temperature range of this separation was between 350 and 420 °C at the heating rate of 30 and 50 °C min^{-1} (Fig. 5 and Table 5). During the third stage, which ranged from 400 to 560 °C, there was a small amount of weight loss (~10%) at a slower rate. The weight loss in the third stage was very much lower as compared with the second stage and also as compared with weight loss during the third stage in an inert atmosphere. Also, the third stage in the oxidizing atmosphere had a very narrow temperature range as compared with the third stage in the inert atmosphere. This suggests that the third stage in the inert and oxidizing atmospheres were different.

The trend of the TGA plot of corn stover in an air atmosphere was very similar to the TGA plot of rice husk in an oxygen atmosphere performed by Mansaray and Ghaly [5]. This suggested that the amount of oxygen in the air atmosphere in our experiment was sufficient for oxidation of a small amount of corn stover particles (~5–10 mg). However, the weight loss in the third stage of corn stover was less than that of rice husk. This may have been due to the smaller amount of lignin in corn stover (10–13%) as compared with rice husk (~20%).

4.2.1. *Parameters of reaction kinetics*

Kinetics of weight loss in air atmosphere at a heating rate of 10 °C min^{-1} was similar to that in nitrogen atmosphere (Table 6). But, at higher rates of 30 and 50 °C min^{-1} the reaction during the second stage occurred very rapidly and activation energies (125–140 kJ mol^{-1}) were higher than activation energies in nitrogen atmosphere (58–63 kJ mol^{-1}).

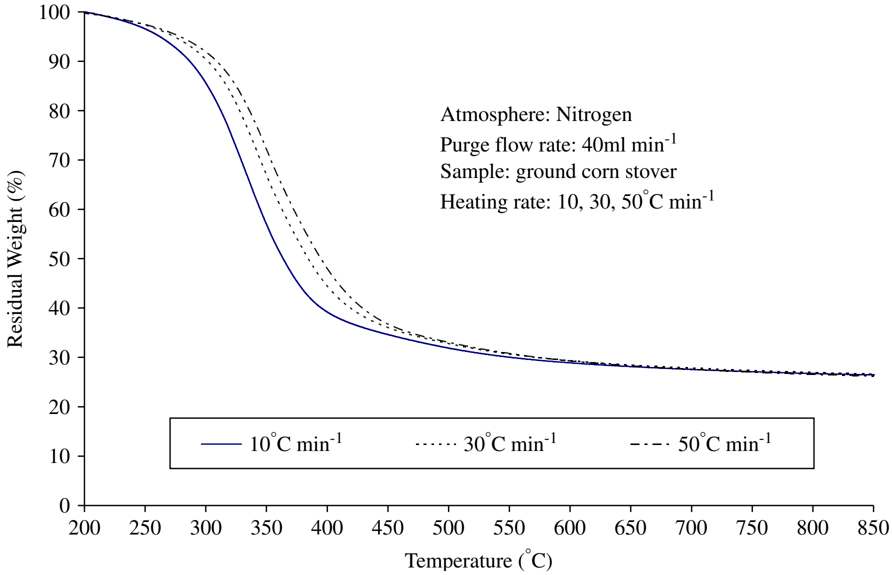

Fig. 3 – Effect of heating rates on TGA plot of corn stover in a nitrogen atmosphere.

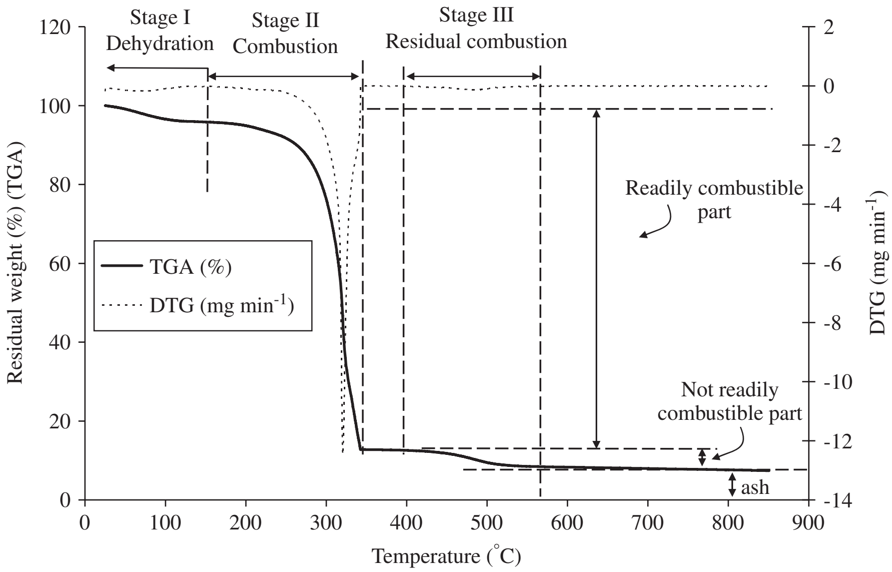

Fig. 4 – Typical TGA plot of corn stover in an air atmosphere.

Table 5 – Temperature range and weight loss in an air atmosphere

	10 °C min^{-1}		30 °C min^{-1}		50 °C min^{-1}	
	Temperature (°C)	Wt (%)	Temperature (°C)	Wt (%)	Temperature (°C)	Wt (%)
Stage I	25	100	25	100	25	100
	115	96.61	135	95.96	130	96.42
Stage II	220	93.85	245	92.22	250	92.55
	400	31.03	350	12.76	350	13.19
Stage III	400	31.03	410	12.49	430	12.88
	540	7.99	560	8.48	565	10.30
Ash+fixed carbon	850	6.88	850	7.43	850	9.75

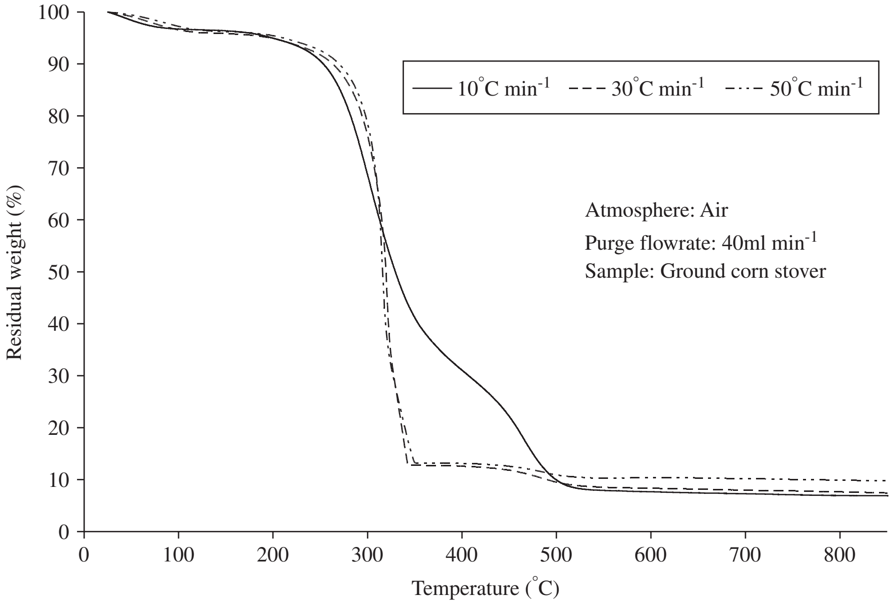

Fig. 5 – Effect of heating rates on thermogravimetric plot of corn stover in an air atmosphere.

Table 6 – Kinetic parameters during second stage in an air atmosphere

	A (s^{-1})	E ($kJ\,mol^{-1}$)	n	r^2
10 °C min^{-1}	1.92×10^4	57.32	0.75	0.81
30 °C min^{-1}	1.12×10^{11}	125.59	0.53	0.96
50 °C min^{-1}	3.32×10^{12}	139.13	0.76	0.92

4.2.2. *Effect of heating rate*

Similar to inert atmosphere, the heating rate (temperature scan rate) tended to slightly increase the start and end temperatures of each stage (Fig. 5 and Table 5). At a slow heating rate of 10 °C min^{-1}, the weight loss was similar to the weight loss at the higher heating rates of 30 or 50 °C min^{-1} up to the first stage of weight loss (Fig. 5). However, beyond that the weight loss for the 10 °C min^{-1} heating rate was unexpectedly different than at higher heating rates in an air atmosphere. At the slow heating rate of 10 °C min^{-1}, the weight loss (63%) during the second stage was lesser than the corresponding weight loss (80%) at the higher heating rate, which suggests that the combustion of corn stover at 10 °C min^{-1} was incomplete up to 420 °C. The rate of weight loss at 10 °C min^{-1} was also much lower than the rate of weight loss at the higher heating rates of 30 and 50 °C min^{-1}. The residual weight losses of 23% and 3–4% then occurred during the third stage of slow and fast heating rates, correspondingly.

5. Conclusions

TGA of corn stover in an inert (nitrogen) atmosphere suggests that there were three distinct stages of weight loss. The first stage ranged from 25 to 125 °C, the second stage from 250 to 450 °C and the third stage from 420–470 to 850 °C. The second stage (active pyrolysis zone) was very close to a first-order reaction. The activation energy of this stage was approximately 60 kJ mol^{-1}.

The weight losses in the oxidizing atmosphere also had three stages. The first stage (25–125 °C) was similar to that in the inert atmosphere. The second stage, however, in this case occurred very rapidly and contributed to most of the weight loss (around 70%). The third stage, which ranged from 400 to 560 °C, contributed to 10% of the weight loss.

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