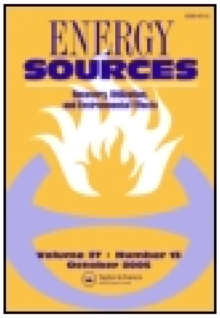

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/ueso20

Thermal Degradation Kinetics of Distillers Grains and Solubles in Nitrogen and Air

L. Wang [a] , A. Kumar [b] , M. A. Hanna [b] , C. L. Weller [b] & D. D. Jones [b]

[a] Department of Natural Resources and Environmental Design, North Carolina Agricultural & Technical State University, Greensboro, North Carolina, USA

[b] Industrial Agricultural Products Center, Department of Biological Systems Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, USA

Version of record first published: 03 Apr 2009.

To cite this article: L. Wang , A. Kumar , M. A. Hanna , C. L. Weller & D. D. Jones (2009): Thermal Degradation Kinetics of Distillers Grains and Solubles in Nitrogen and Air, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 31:10, 797-806

To link to this article: http://dx.doi.org/10.1080/15567030701752743

Energy Sources, Part A, 31:797–806, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1556-7036 print/1556-7230 online
DOI: 10.1080/15567030701752743

Thermal Degradation Kinetics of Distillers Grains and Solubles in Nitrogen and Air

L. WANG,[1] A. KUMAR,[2] M. A. HANNA,[2] C. L. WELLER,[2] and D. D. JONES[2]

[1]Department of Natural Resources and Environmental Design, North Carolina Agricultural & Technical State University, Greensboro, North Carolina, USA
[2]Industrial Agricultural Products Center, Department of Biological Systems Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, USA

Abstract *The pyrolysis and oxidation kinetics of distillers grains and solubles were determined using thermogravimetric analysis . The starting temperature of pyrolysis and oxidation of distillers grains and solubles increased with the increase of heating rate and initial moisture content. The pyrolysis and oxidation of distillers grains and solubles were completed at 650°C and 850°C, respectively, which were independent of the heating rate and the initial moisture content. The residual weights of distillers grains and solubles after pyrolysis and oxidation were 27.15% and 5.49% of the original dry mass of distillers grains and solubles. Thermogravimetric analysis data was used to determine kinetic parameters of the thermal degradation of distillers grains and solubles. Predicted dynamic residual weights of distillers grains and solubles during thermal degradation agreed well with experimental data.*

Keywords biomass, distillers grains and solubles, kinetics, TGA, thermochemical conversion

1. Introduction

Dry-grind ethanol production continues to expand in the United States. During dry-grind ethanol production, approximately one-third of the mass of grain feedstock (i.e., ~0.8 kg/liter) resides in distillers grains and solubles (DGS) as by-products. DGS are a renewable source for production of high-value chemicals such as policosanols, phytosterols, and free fatty acids (Wang et al., 2005). The economic value of DGS would likely increase if the high-value compounds were extracted from the DGS and the solid residue after extraction was further converted to liquid and gaseous fuels and chemicals.

Thermochemical conversion methods mainly including combustion, pyrolysis, and gasification provide a competitive way to produce chemical and energy products from low-value biomass such as the DGS residue after extraction (Demirbas et al., 2006). Thermal degradation kinetics play key roles in design, operation and modeling of a thermochemical conversion process. Thermogravimetric analysis (TGA) has been used extensively to determine the thermal degradation characteristics and kinetic parameters of biomass during thermochemical conversion (Mansaray and Ghaly, 1999; Degirmenci and Durusoy, 2002). Degirmenci and Durusoy (2002) investigated the effects of heating

Address correspondence to Lijun Wang, Department of Natural Resources and Environmental Design, North Carolina Agricultural & Technical State University, Greensboro, NC 27411. E-mail: lwang@ncat.edu

rate on pyrolysis characteristics and kinetic parameters of oil shale using TGA. Mansaray and Ghaly (1999) determined the oxidation kinetic parameters of rice husks in oxygen using TGA. However, little published research has been found on the effects of heating rate and initial moisture content of biomass on its thermal degradation. Particularly, no published research has been found on drying, pyrolysis, and oxidation characteristics and kinetic parameters of DGS during thermal degradation. Therefore, the objective of this study was to determine the thermal degradation characteristics and kinetic parameters of DGS during drying, pyrolysis, and oxidation, and to investigate the effects of heating rate and initial moisture content of DGS on its thermal degradation using TGA.

2. Materials and Methods

2.1. *Distillers Grain Particles*

DGS were obtained from a local ethanol production facility in Nebraska. The average particle size of DGS were 800 μm. Particle size was calculated from the weight and the average particle size of each fraction obtained using a sieve shaker (Ro-TAP, W.S. Tyler, Cleveland, Ohio) equipped with six sieves (U.S. standard sieve Nos. 12, 14, 16, 20, 35, and 140) and a pan. Before conducting thermal degradation experiments, lipids in DGS were extracted using a Soxhlet extractor (Foss Tecator Soxtec HT 6, Fisher Scientific, Pittsburgh, PA) with *n*-hexane as the solvent for 12 h. The moisture content of DGS residue after extraction of lipids was 1.36% by weight (wet basis), which was determined using a moisture analyzer (HG 53 moisture analyzer, Mettler-Toledo GmbH, Laboratory and Weighing Technologies, Greifensee, Switzerland). The DGS residues after extraction of lipids were stored in a glass vial for TGA.

2.2. *Thermogravimetric Analysis*

Thermal degradation was conducted on a thermogravimetric analyzer (Perkin-Elmer TGA 7, Norwalk, CT). Approximately 15–25 mg of DGS was used for each analysis. For determining the drying characteristics, the moisture contents of DGS were adjusted to be 45% (wet basis) by adding a given amount of distilled water. Nitrogen and air at a flow rate of 20 ml/min were used as the purging gases for pyrolysis and oxidation analyses, respectively. The temperature of DGS samples was increased from the ambient temperature of 20°C to 650°C for the pyrolysis analysis and from 20°C to 850°C for the oxidation analysis at heating rates of 10, 30, and 50°C/min. Dynamic residual weight and temperature of DGS were recorded and analyzed by a computer using TGA7 software. The TGA data were used to determine the initial degradation temperature, degradation rate, residual weight at the end of degradation, and degradation kinetic parameters.

2.3. *Thermal Degradation Kinetics*

During thermal degradation of biomass, the biomass initially experiences drying to release moisture and then pyrolysis to release organic volatiles followed by gasification and combustion in the presence of an oxidizing agent. The overall reactions of DGS in nitrogen and air include:

1. Drying (in nitrogen and air): wet DGS $\rightarrow$ dried DGS + water
2. Pyrolysis (in nitrogen): dried DGS $\rightarrow$ *Ash* + *Char* + volatiles
3. Oxidation (in air): dried DGS + O_2 $\rightarrow$ *Ash* + CO_2 + H_2O

The drying, pyrolysis and oxidation kinetics of DGS can be expressed as (Mansaray and Ghaly, 1999; Degirmenci and Durusoy, 2002):

$$\frac{dX}{dt} = -Ae^{-\left(\frac{E}{RT}\right)}X^n, \tag{1}$$

where X is dimensionless sample weight, t is time (s), R is universal gas constant (8.314 kJ mol^{-1} K^{-1}), and T is absolute temperature (K).

The TGA data (the relationship between residual weight, w, and temperature, T, and time, t) were used to determine kinetic parameters of pre-exponential factor, A (min^{-1}), activation energy, E (kJ mol^{-1}) and reaction order, n in Eq. (1). To determine the kinetic parameters from TGA data, Eq. (1) was transformed to its linear form:

$$\ln\left[\left(-\frac{1}{w_i - w_f}\right)\left(\frac{dw}{dt}\right)\right] = \ln(A) + \left(\frac{E}{R}\right)\cdot\left(\frac{1}{T}\right) + n\ln\left(\frac{w - w_f}{w_i - w_f}\right), \tag{2}$$

where w, w_i, and w_f are residual weight and initial and final weights of sample ($X = (w - w_f)/(w_i - w_f)$).

3. Results and Discussion

3.1. Pyrolysis Characteristics

TGA of pyrolysis rate of DGS residue with 1.36% of moisture (wet basis) in nitrogen at heating rates of 10, 30, and 50°C/min is shown in Figure 1. At the heating rates of 10, 30, 50°C/min, the starting pyrolysis temperatures were 180°C, 200°C, 220°C,

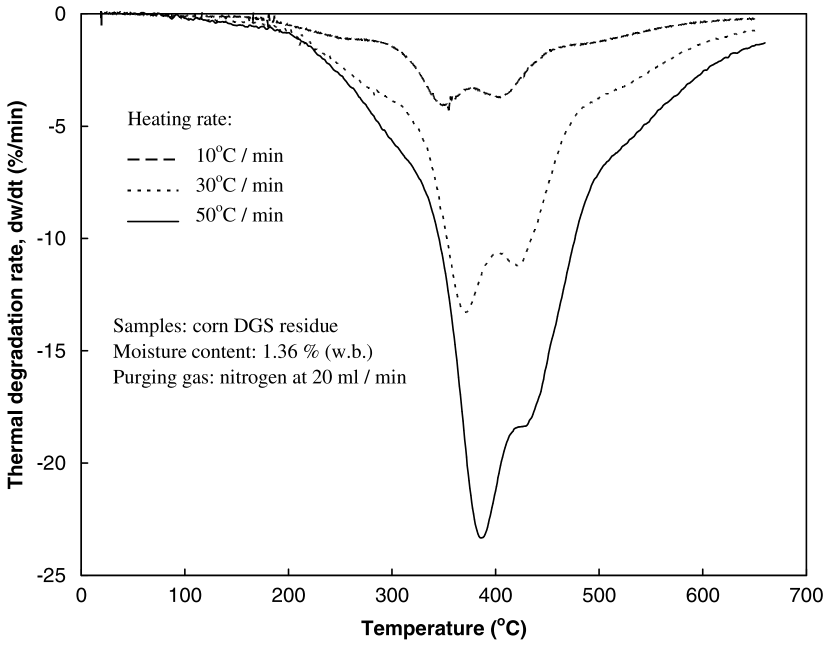

Figure 1. Thermogravimetric analyses of pyrolysis rate of DGS residue in nitrogen at different heating rates.

respectively, as shown in Figure 1. Before pyrolysis, drying occurred to remove the water in DGS. The drying process was affected by the initial moisture content, drying time, and drying temperature. The time for DGS samples to reach a given temperature decreased with an increase in heating rate. The end drying temperature or the starting pyrolysis temperature thus increased with the increase of heating rate to remove a given amount of moisture from the samples. The pyrolysis rate increased with the increase in the heating rate for the DGS with the same moisture content as shown in Figure 1. The maximum pyrolysis rate of DGS with 1.36% moisture in nitrogen at the heating rate of 50°C/min was 23%/min (wet basis), which was about 6 times of the value at the heating rate of 10°C/min. For the heating rates at 10, 30, and 50°C/min, the maximum pyrolysis rates of DGS in nitrogen was achieved at the temperature from 350°C to 390°C. The temperature for the maximum pyrolysis rate slightly increased with the increase of heating rate. Degirmenci and Durusoy (2002) also observed that both the temperature for the maximum decomposition rate and the maximum decomposition rate increased with heating rate for the pyrolysis of oil shale using TAG.

The weight loss of DGS during thermal degradation is a function of degradation rate and degradation time. At higher heating rate, although the degradation rate was higher, the time to reach a given temperature became shorter and the residual weight at a given temperature during thermal degradation may be higher as shown in Figure 2. However, whatever the heating rate was, the residual weights of DGS in nitrogen at 650°C almost became constant at 27.15 ± 0.04% of the original dry mass of DGS with 1.36% moisture as shown in Figure 2. Therefore, the pyrolysis of DGS with 1.36% moisture in nitrogen was complete at 650°C, which was independent of the heating rate. The remaining solid residue after complete pyrolysis was char and ash.

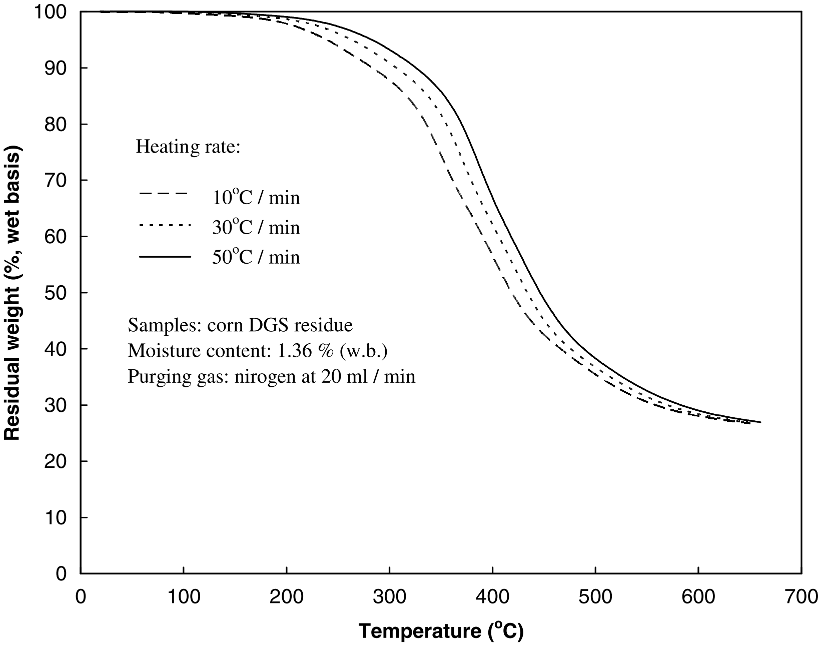

Figure 2. Dynamic residual weights of DGS residue during pyrolysis in nitrogen at different heating rates.

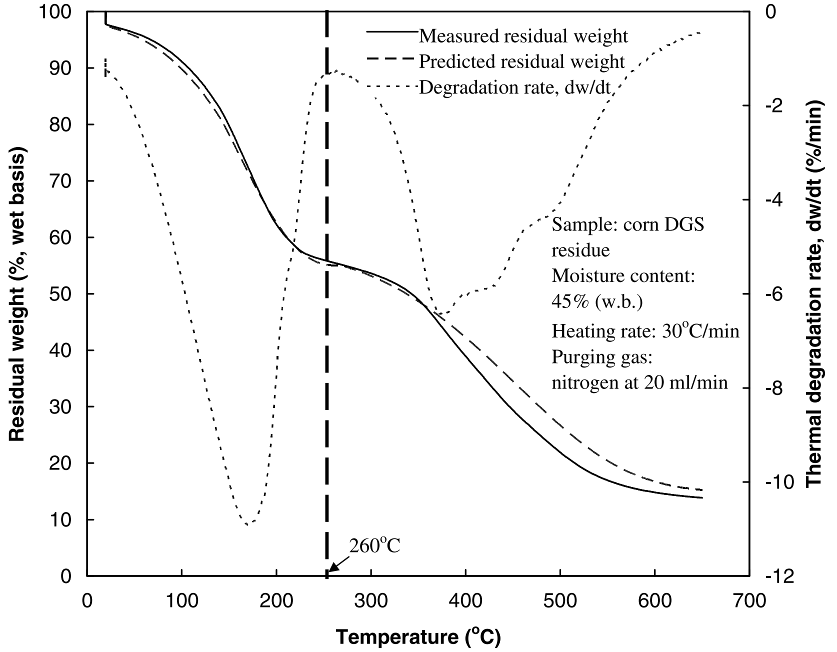

Figure 3. Thermogravimetric analysis of thermal degradation of DGS residue with 45% moisture by wet basis in nitrogen.

TGA of thermal degradation of DGS residue with 45% moisture by wet basis in nitrogen is shown in Figure 3. For the DGS sample with 45% moisture (wet basis) at a heating rate of 30°C/min, there are two obvious degradation zones: the drying zone from ambient to 260°C and the pyrolysis zone from 260°C to 650°C. At the heating rate of 30°C/min, the stating temperature of pyrolysis of DGS with 45% moisture was 260°C as shown in Figure 3, compared to 200°C for the sample with 1.36% moisture at the same heating rate as shown in Figure 1. Increasing the moisture content of DGS increases the total drying time at the same heating rate and thus increases the end temperature of drying or starting temperature of pyrolysis. For the DGS sample with 45% moisture, the residual weight of DGS in nitrogen at 650°C became constant around 25% of the original dry mass of DGS as shown in Figure 3. The slight decrease in residual weight after pyrolysis for the sample with higher moisture content might be caused by the reaction between steam vapor and char generated from DGS during thermal degradation.

3.2. Oxidation Characteristics

TGA of oxidation rate of DGS residue with 1.36% moisture in air at heating rates of 10, 30, and 50°C/min is shown in Figure 4. There were two obvious oxidation zones as shown in Figure 4. The starting temperatures of the first and second oxidation zones increased slightly from 180°C to 220°C, and from 470°C to 490°C, respectively, with the increase of heating rate. As shown in Figure 4, the maximum oxidation rate at the first zone was much higher than that of the second zone. The maximum oxidation rates of the first and second zones at the heating rate of 50°C/min were 46.5%/min and 6.5%/min (wet basis), which were about 10 and 5 times the values at the heating rate of 10°C/min,

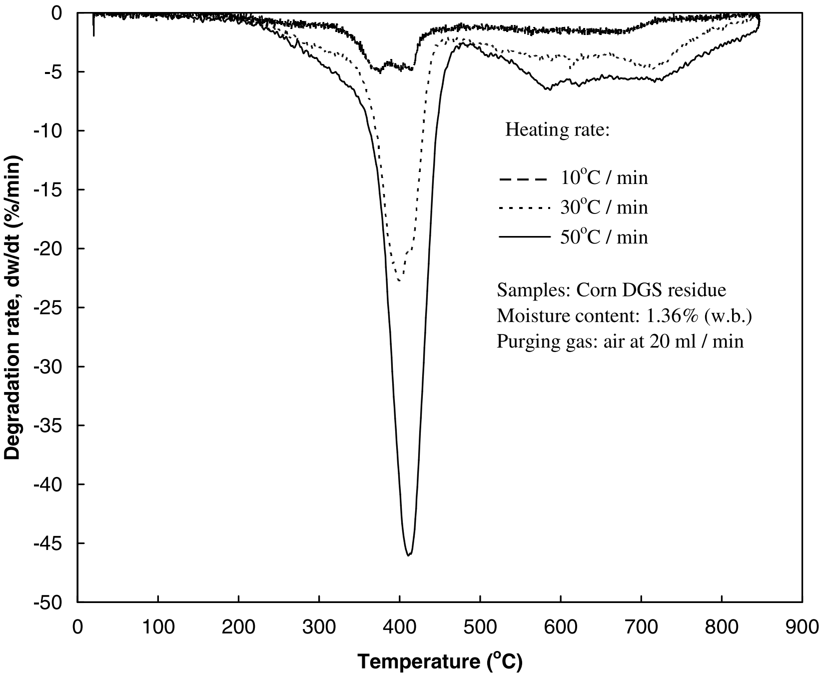

Figure 4. Thermogravimetric analysis of oxidation rate of DGS residue in air at different heating rates.

respectively. At the first zone, some volatiles in DGS were released and oxidized at a low temperature and high rate. At the second zone, the char and more thermally stable components, such as lignin, continued to be oxidized at higher temperatures and lower rates. The temperatures for the maximum oxidation rates of the first and second zones were in the range from 375°C to 415°C, and from 690°C to 730°C, respectively. The temperatures for the maximum oxidation rates slightly increased with increasing heating rates as shown in Figure 4.

As shown in Figure 5, whatever the heating rate was, the residual weight of DGS in air at the end of the first oxidation zone was almost constant at 42.57 ± 2.75% of the original dry mass of DGS with 1.36% moisture. The remaining solid residue at the end of the first oxidation zone may have been char and more thermally stable components such as lignin in the DGS. With a further increase in temperature to 850°C, the residual weight almost became constant at 5.49 ± 0.03% of the original dry mass of DGS. Therefore, the oxidation of DGS in air was complete at 850°C, which was independent of the heating rate. The remaining solid residue at the end of the second oxidation zone was ash.

TGA of thermal degradation of DGS residue with 45% moisture by wet basis in air is shown in Figure 6. There are three obvious degradation zones for the DGS sample with 45% moisture in air at a heating rate of 30°C/min as shown in Figure 6: the drying zone from ambient to 260°C, the first oxidation zone from 260°C to 525°C, and the second oxidation zone from 525°C to 850°C. At the heating rate of 30°C/min, the starting temperatures of the first and second oxidation zones of DGS with 45% moisture were 260°C and 525°C, respectively, as shown in Figure 6, compared to 200°C and 470°C for the sample with 1.36% moisture at the same heating rate as shown in Figure 4. The

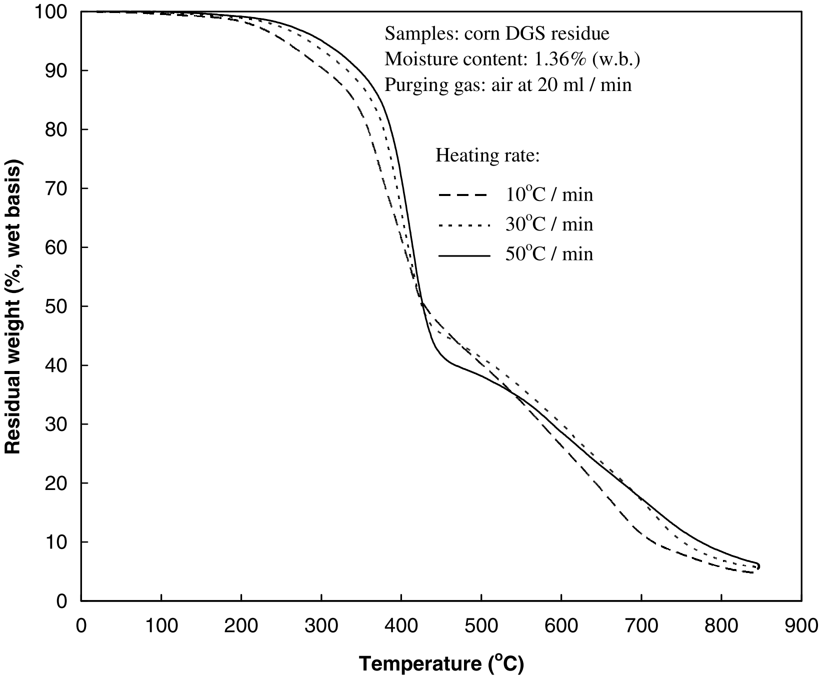

Figure 5. Dynamic residual weights of DGS residue during oxidation in air at different heating rates.

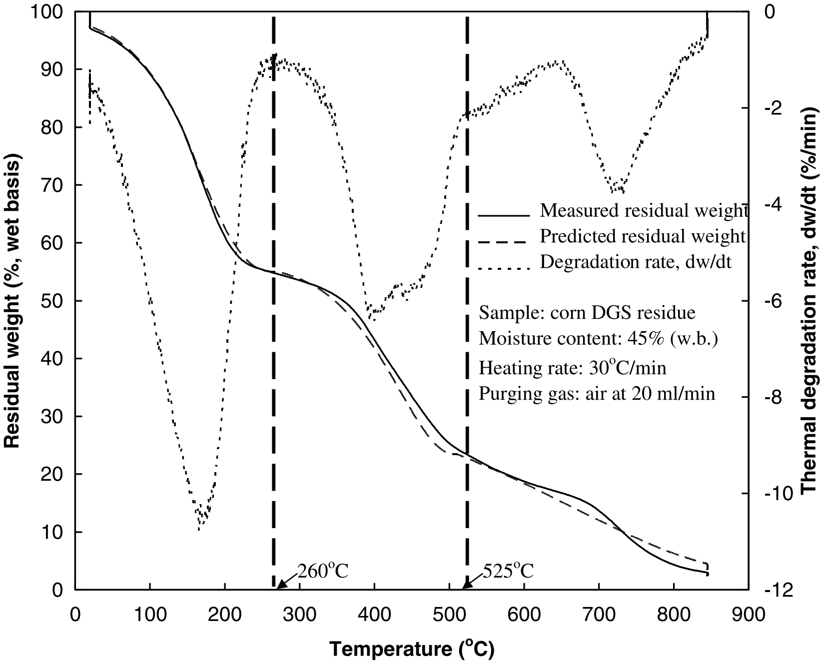

Figure 6. Thermogravimetric analysis of thermal degradation of DGS residue with 45% moisture by wet basis in air.

starting temperatures of the first and second oxidation zones for the DGS sample with 45% moisture shifted to higher temperatures because more moisture was evaporated from the sample before oxidation. The initial moisture content of DGS had no significant effect on the residual weights at the end of the first and second zones. For oxidation of DGS with 45% moisture in air at a heating rate of 30°C/min, the remaining solid residues at the end of the first and second oxidation zone were 42.34% and 4.5% of the original dry mass of DGS, respectively, as shown in Figure 6.

3.3. *Kinetic Parameters*

The TGA data were used to determine the pre-exponential factor, activation energy, and reaction order in the kinetic model given in Eq. (1). It was found that the natural logarithms of the pre-exponential factors, the activation energies and the reaction orders for pyrolysis, and the first and second oxidation zones had linear relationships with heating rate. The correlation equations obtained from the linear regressions of pre-exponential factors, activation energies, and reaction orders with heating rate are given in Table 1. The pre-exponential factors, activation energies, and reaction orders for both pyrolysis and oxidation increased with increases in heating rate as shown in Table 1. As seen in Figures 3 and 6, DGS residue had similar drying characteristics in both nitrogen and air. The TGA data for the DGS samples with 45% moisture before pyrolysis and oxidation were used to determine the pre-exponential factor, activation energy, and reaction order of drying kinetics given in Table 1.

3.4. *Comparison of Experimental and Predicted TGA Curves*

The kinetic models of drying, pyrolysis, and oxidation were used to predict the dynamic residual weights during thermal degradation of DGS. The comparison between predicted and measured dynamic residual weights of DGS with 45% moisture during pyrolysis in nitrogen and oxidation in air are given in Figures 3 and 6. The predicted dynamic residual weights of DGS using the kinetic models were in good agreement with the experimental values as shown in Figures 3 and 6. The average standard deviations between predicated and experimental of dynamic residual weight of DGS were 1.27 for the pyrolysis and 0.70 for the oxidation. The slight overestimation of residual weight for the pyrolysis of DGS may have been caused by neglecting the effect of moisture on the pyrolysis rate.

4. Conclusions

TGA was used to determine the thermal degradation characteristics and kinetic parameters of DGS residue in nitrogen and air. TGA indicated that the starting temperatures of pyrolysis of DGS in nitrogen and oxidation in air increased with the increase of heating rate and initial moisture content. There were two obvious oxidation zones during oxidation of DGS in air. The oxidation rate of the first zone was much higher than that of the second zone. The pyrolysis and oxidation rates increased with the heating rate. The pyrolysis and oxidation of DGS were completed at 650°C and 850°C, respectively, which were independent of the heating rate. The residual weights of DGS after pyrolysis in nitrogen and oxidation in air were 27.15% and 5.49% of the original dry mass of DGS. The natural logarithm of pre-exponential factors, the activation energies and the reaction orders determined by the TGA data for pyrolysis, and the first oxidation zone and the second oxidation zone had linear relationships with the heating rate. The kinetic models

Table 1

Kinetic parameters for thermal degradation of DGS in nitrogen and air

	Heating rate, q, °C/min	Final residual, %, dry basis	Pre-exponential factor, A, min^{-1}	Activation energy, E, kJ mol^{-1}	Reaction order, n, –
Drying	30	—	64.45	18.51	0.69
Pyrolysis (in nitrogen)	10	27.13	8.9	27.5	0.83
	30	27.13	59.5	32.3	0.86
	50	27.20	180.1	36.1	0.89
		27.15 ± 0.04	$A = \exp(0.0752q + 1.5637)$	$E = 0.2139q + 25.533$	$n = 0.0015q + 0.8171$
Oxidation in air (the first reaction zone)	10	44.06	75.9	37.5	0.47
	30	44.25	6,138.5	54.3	0.62
	50	39.40	32,869.1	61.3	0.71
		42.57 ± 2.75	$A = \exp(0.1518q + 13.2644)$	$E = 0.5953q + 33.190$	$n = 0.0059q + 0.4212$
Oxidation in air (the second reaction zone)	10	5.49	0.2	11.8	0.44
	30	5.46	10.3	31.5	0.67
	50	5.52	19.2	32.8	0.73
		5.49 ± 0.03	$A = \exp(0.1105q - 2.0399)$	$E = 0.5260q + 9.5977$	$n = 0.0072q + 0.3952$

were used to predict the dynamic residual weight of DGS during pyrolysis in nitrogen and oxidation in air. The predictions agreed well with the experimental data.

Acknowledgments

A contribution of the University of Nebraska Agricultural Research Division, supported in part by funds provided through the Hatch Act, USDA. Mention of a trade name, proprietary products, or company name is for presentation clarity and does not imply endorsement by the authors or the University of Nebraska. The authors wish to thank Dr. Yuris Dzenis and Dr. Yongkui Wen for their support in TGA analyses.

References

Degirmenci, L., and Durusoy, T. 2002. Effect of heating rate on pyrolysis kinetics of goynuk oil shale. *Energy Sources* 24:931–936.

Demirbas, A., Ozturk, T., and Demirbas, M. F. 2006. Recovery of energy and chemicals from carbonaceous materials. *Energy Sources Part A* 28:1473–1482.

Mansaray, K. G., and Ghaly, A. E. 1999. Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis. *Biomass & Bioenergy* 17:19–31.

Wang, L. J., Weller, C. L., and Hwang, K. T. 2005. Extraction of lipids from grain sorghum DDG. *Trans. ASAE* 48:1883–1888.