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Determination of Reaction Kinetics of Barley Straw Using Thermogravimetric Analysis

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ABSTRACT

Reaction kinetics of three varieties of barley straw (Kadeth, Laurier, and Leger) were studied at a heating rate of 20°C/min in an oxidizing atmosphere of 15% oxygen and 85% nitrogen using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques. The thermal degradation characteristics and the kinetic parameters (order of reaction, activation energy, and pre-exponential factor) were determined for the two reaction zones from the TGA and DTA curves. Thermal degradation rates in the first reaction zone were relatively higher than those in the second reaction zone. The thermal decomposition of the straw variety Kadeth started at a lower temperature (186°C) than the straw varieties Laurier (229°C) and Leger (223°C). Residual weights recorded at 700°C were in the range of 4.3–7.2%. Higher activation energies (85.4–103.2 kJ/mol) and pre-exponential factors (0.73×10^7–49.10×10^7) were obtained for all varieties of barley straw in the first reaction zone as compared to those of the second reaction zone (34.8–58.6 kJ/mol and 0.27×10^2–14.43×10^2 for the activation energy and pre-exponential factor, respectively). The order of reactions were in the range of 2.0–2.3 and 1.1–1.2 for the first and second reaction zones, respectively.

Index Entries: Kinetics; barley straw; thermogravimetry; oxidizing atmosphere; activation energy; pre-exponential factor; order of reaction.

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INTRODUCTION

Barley is the fourth major cereal crop after wheat (552 million tons/yr), rice (510 million tons/yr) and maize (464 million tons/yr) with a worldwide production of 169 million tons/yr (*1*). Canada, as a world leader in barley production, annually produces over 13 million tones of barley (2). According to Peill (3), the grain:straw ratio for cereal crops such as wheat, barley, oats, and rye is in the range of 1.0:1.2–1.5. Based on this grain:straw ratio, it is estimated that approx 203–253 million tons of barley straw are produced worldwide annually, of which 16–20 million tons are produced in Canada.

In spite of the increasing trend of the cereal straw surplus (wheat, barley, and rice straws in particular), proper methods of disposal and/or utilization of cereal straws have yet to be developed. Today, most of the straw is disposed by direct burning in the field, which results in the loss of energy (18 giga joules/ton) as well as the emission of various pollutants to the atmosphere. However, in the last decade, most of the developed countries imposed new regulations to restrict field burning of straw, primarily for environmental reasons. This, thus, increased the interest in the utilization of straw as a renewable source of energy (*4–12*).

Among the various energy conversion options of cereal straw, thermochemical conversion methods offer the most efficient way of disposing/utilization of straw. However, there is very little information on the kinetics of thermal degradation reactions of straw, which is required for the proper design and modeling of thermochemical conversion systems. Although, some efforts were directed to the study of the thermochemical characteristics of wheat and rice straws (*13–19*), no information was found in the literature on the thermochemical characteristics of barley straw.

OBJECTIVES

The aim of this study was to investigate the kinetics of thermochemical conversion of three common types of barley straws on the basis of their thermal degradation behavior. The specific objectives were:

1. To conduct thermogravimetric and differential thermal analyses on three varieties of barley straws (Kadeth, Laurier, and Leger) at a heating rate of 20°C/min in an oxidizing atmosphere of 15% O_2 and 85% N_2.
2. To determine the thermal degradation rate in the first and second reaction zones, the initial degradation temperature, and the residual weight at 700°C.
3. To determine the kinetic parameters (the order of reaction, the preexponential factor, and the energy of activation) using thermogravimetric curves.

THEORY

Although, thermogravimetric analysis is one of the major thermal analysis techniques used to study the kinetics of thermal decomposition reactions of carbonaceous materials, there is no generally accepted method for determining kinetic parameters from thermogravimetric data (*18, 20–24*). In this study, determination of the kinetic parameters from thermogravimetric data was based on the following rate equation (*25*):

$$(dX / dt) = -A\, e^{-(E/RT)}\, X^{n} \tag{1}$$

where: X is the weight of sample undergoing reaction (kg), t is the time (min), A is the pre-exponential factor (min^{-1}), E is the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), R is the universal gas constant (8.314 $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature (K), and n is the order of reaction (-).

Ergüdenler and Ghaly (*13*) used a technique based on the Arhenius equation of the form presented by Duvvuri et al. (*23*) and Goldfarb et al. (*26*) to determine the kinetic parameters of wheat straw. They applied the least squares technique (multiple linear regression) to the linearized form of Arhenius equation in order to determine the pre-exponenetial factor (A), the activation energy (E), and the order of reaction (n). The simplified form of the linearized rate equation was as follows:

$$y = B + Cx + Dz \tag{2}$$

The parameters y, x, z, B, C, and D in Eq. (2) were defined as follows:

$$\begin{aligned} y &= \ln\{\,[-1/(w_o - w_f)]\,[dw/dt]\,\} \\ x &= 1/(\mathrm{RT}) \\ z &= \ln[(w - w_f) / (w_o - w_f)] \\ B &= \ln A \\ C &= -E \\ D &= n \end{aligned}$$

where: w is the weight of sample at time t (kg), w_f is the weight of the residue (kg), and w_o is the initial weight of the sample (kg).

Ergüdenler and Ghaly (*13*) showed that the rate equation (Eq. [1]) cannot be used in its present form to predict the thermal degradation for the entire temperature range; the kinetic parameters determined for the second reaction zone under-predicted the thermal degradation results in this zone. They, therefore, modified the rate equation as follows:

$$(dX / dt) = -C\,A\, e^{-(E/RT)}\, X^{n} \tag{3}$$

The authors concluded that the thermal degradation of various varieties of straw can be predicted with high accuracy for the entire temperature range if the proper values of the factor "C" ar used for both the first and second reaction zones.

Table 1
Characteristics of Barley Straw

Characteristics	Variety of straw		
	Kadeth	Laurier	Leger
Proximate analysis,[a] %			
Volatile matter	73.83	82.41	81.48
Fixed carbon	18.84	13.29	14.30
Ash	7.32	4.30	4.22
Ultimate analysis,[a] %			
C	44.54	45.47	46.01
H	5.12	5.61	5.45
O	41.59	44.57	44.07
N	0.82	0.20	0.39
S	0.19	0.12	0.10
Cl	0.33	0.01	0.01
Ash	7.41	4.02	3.97
Lower heating value, MJ/kg	17.07	17.76	18.20

[a] Weight percentage on dry basis.

MATERIALS AND METHODS

Straw Collection

Three varieties of barley straws (Kadeth, Laurier, and Leger) were selected for the thermogravimetric and differential thermal analyses. Straw samples were obtained from harvested fields of Dyke View Farms at Port Williams, Nova Scotia. Samples of approx 5 kg of straw were collected from each field shortly after harvest, placed in polyethylene bags, and transported to the Thermal Analysis Laboratory at the Technical University of Nova Scotia in Halifax. The straws were dried in an air-forced oven at 105°C on the same day to avoid deterioration owing to moisture content. The dried straws were stored in polyethylene bags until needed for further processing. Some characteristics of the three varieties of barley straw are given in Table 1.

Sample Preparation

Dried straw samples of 1 kg each were first coarse-ground through a 20-mesh sieve on a medium-size Wiley Mill (Brook Crompton Parkinson Limited, Model No. X876249, Toronto, Ontario). The coarse-ground materials were reground through a 40-mesh sieve on the Wiley Mill in order to narrow the range of the particle size and, thus, obtain homogenous samples. These were stored in air-tight plastic containers until needed for the thermogravimetric analyses. This procedure ensured reproducible thermogravimetric results.

Thermal Analysis

Straw samples were subjected to thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in an oxidizing atmosphere of 15% O_2 and 85% N_2 using a heating rate of 20°C/min. METTLER Thermal Analyzer (TG 50 and DSC 30) was used for the thermal analyses. Owing to the variation of impurities in the laboratory air and the limitations on the quality of the gas to be used by the thermal analyzer, a high-purity oxidizing gas (Linde Union Carbide, Cat. No. 105338, Toronto, Ontario), which is close in composition to air, was used in the experiments.

In order to ensure the uniformity of the temperature of the sample, a small sample of size is recommended (*25*). However, if the sample material is nonhomogeneous, a large sample size becomes necessary. In this study, several sample sizes were analyzed in order to obtain information on temperature uniformity. A good reproducibility was achieved with a sample size as small as 10 mg. Therefore, samples weighing approx 10 mg were used throughout the study.

The TG50 Thermobalance consisted of a microbalance that has a precision of $\pm 0.1\ \mu g$. The base with the furnace was controlled by a TA Processor. The furnace temperature in the TG50 Thermobalance was controlled in such a way that the sample temperature follows the desired profile. For this purpose, the temperature equilibration function between the furnace and the sample was provided by the manufacturer (Metler Instrument AG, Greinfensee-Zurich, Switzerland). Besides the shape and color of the sample, the heat transfer rate is principally dependent on the furnace temperature and the heat capacity of the sample. However, the coefficients of the temperature equilibration function that are specific to the sample have been proven to be constant for small samples and equal to the standard values given by the manufacturer of the instrument. The precision of the temperature measurement for TG50 Thermobalance is ±2°C. For a higher temperature homogeneity in the sample, platinum crucibles with volume of 0.07 mL were used.

The samples were heated from the ambient temperature to 700°C. A continuous recording of weight loss and temperature was obtained. The data were analyzed to determine the thermogravimetric and differential thermal analyses indices (thermal degradation rates in the two reaction zones, the initial degradation temperature, the residual weight at 700°C, and the peak temperature and peak area for the two exothermic reactions).

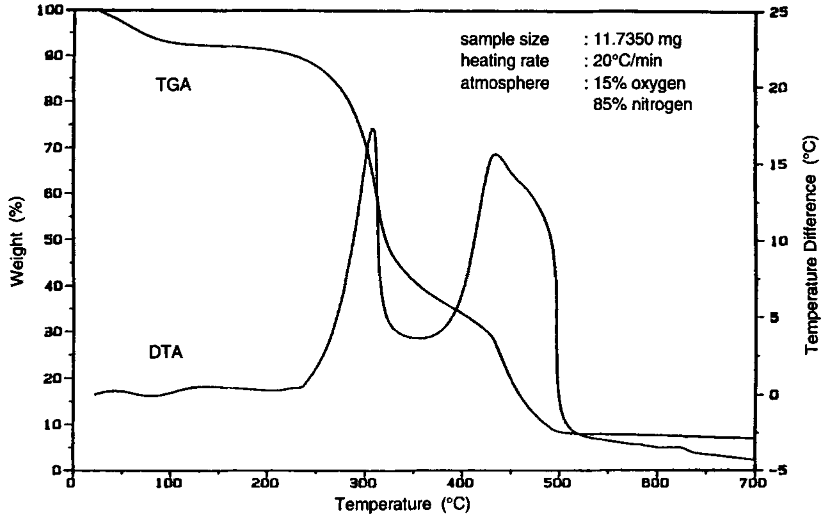

Fig. 1. The thermogravimetric and differential thermal analyses results obtained for the Kadeth variety of barley straw.

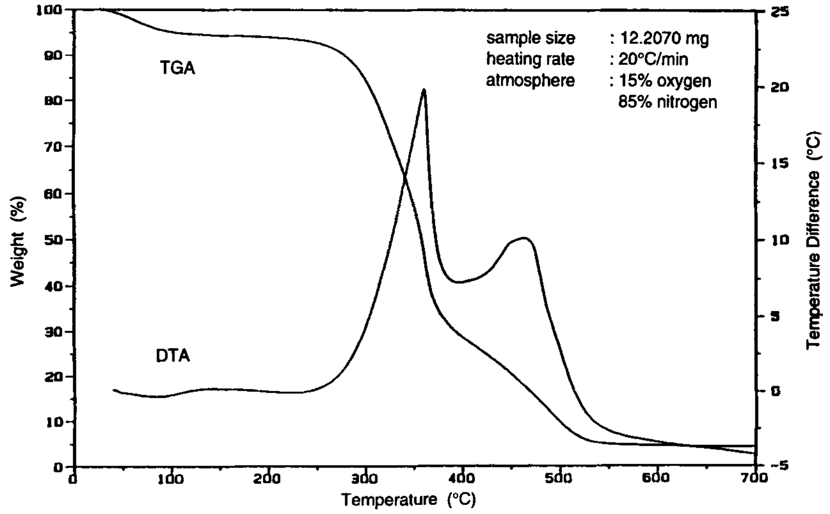

Fig. 2. The thermogravimetric and differential thermal analyses results obtained for the Laurier variety of barley straw.

RESULTS AND DISCUSSION

The thermogravimetric and differential thermal analyses results obtained for three varieties of barley straw (Kadeth, Laurier, and Leger) are given in Figs. 1-3. The thermogravimetric curves were used to determine the kinetic parameters of each variety of barley straw. The differential thermal analyses curves showed how exothermic or endothermic the thermal degradation reactions were. The two-step nature of the thermogravimetric curves and the dual peak characteristics of the DTA curves

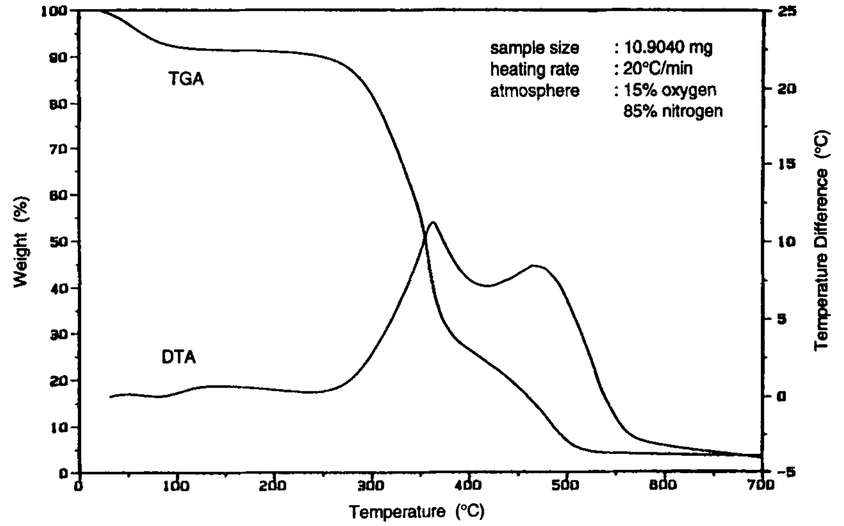

Fig. 3. The thermogravimetric and differential thermal analyses results obtained for the Leger variety of barley straw.

Table 2
Differential Thermal Analysis

Type of straw	Exothermic peaks: First peak T, °C	First peak Δ T, °C	Second peak T, °C	Second peak Δ T, °C	Peak area, °C/min-mg
Kadeth	311	17.3	436	15.6	10.2
Laurier	364	19.9	465	10.1	10.2
Leger	367	11.2	472	8.5	8.7

T = temperature.
Δ T = temperature difference resulting from exothermic reactions.

showed that barley straw has two distinct reaction zones. Therefore, kinetics and thermal degradation characteristics of the two zones were investigated separately.

Differential Thermal Analysis

The results of differential thermal analysis are summarized in Table 2. The DTA curves showed that two overlapping reactions took place between 220 and 550°C for all straw varieties. The first exothermic reactions started at a temperature slightly over 220°C and reached their peak values at the temperatures of 311, 364, and 367°C for the straw varieties Kadeth, Laurier, and Leger, respectively. The temperature difference owing to exothermic reactions in the first zone were in the range of 11.2–19.9°C. The second exothermic reactions started at a temperature 30–50°C higher than the temperature at which the first reaction peak was observed, and reached their peak values at the temperatures of 436, 465, and 472°C for straw varieties Kadeth, Laurier, and Leger, respectively. The temperature differences resulting from the exothermic reactions in the second reaction zone were lower than those of the first zone. The highest temperature difference was obtained for the straw variety Kadeth (15.6°C) followed by Laurier (10.1°C) and Leger (8.5°C) straw varieties.

Thermogravimetric Analysis

The results of thermal degradation of barley straws in the first reaction zone are summarized in Table 3. Increasing the temperature from ambient to 700°C, resulted in weight losses of 7.1–9.3% resulting from the evaporation of water (moisture) in the straw. The initial decomposition of the Kadeth straw variety started at a lower temperature (186°C) compared to the straw varieties Laurier (229°C) and Leger (223°C). Initially, the thermal degradation rates of the straws were slow. However, at temperatures in excess of 250°C very rapid degradation of the straws was observed. Average degradation rates of 6.5, 7.9, and 7.7%/min; and maximum degradation rates of 22.9, 19.6, and 24.5%/min were obtained for the straw varieties Kadeth, Laurier, and Leger, respectively. The final temperature of the first reaction zone was lower for Kadeth straw variety (330°C) than those of Laurier (377°C) and Leger (385°C) straw varieties. Therefore, the total degradation in the first zone for the Kadeth straw variety (46.5%) was relatively lower compared to those of Laurier (58.1%) and Leger (62.6%) straw varieties.

The results of thermal degradation in the second reaction zone are summarized in Table 4. The end of the first reaction zone was accepted as the beginning of the second reaction zone. The thermal degradation rates were lower in the second reaction zone compared to those of the first reaction zone for all straw varieties. The average degradation rates of Laurier, Leger, and Kadeth straw varieties were 3.6, 3.7, and 4.6%/min, respectively. The maximum degradation rate of Kadeth straw variety (10.0%/min) was much higher than those of Laurier (4.3%/min) and Leger (5.2%/min) straw varieties. The total decomposition in the second zone for Kadeth straw variety (38.4%) was, also, higher than those of Laurier (29.5%) and Leger (23.8%) straw varieties. Thermal degradation of the straw samples was almost complete at the end of the second zone. The final temperatures of the second zone were 498, 539, and 513°C for Kadeth, Laurier, and Leger straw varieties, respectively. At temperatures above 520–540°C, an insignificant decomposition of the straws was observed. The residual weights of Kadeth, Laurier, and Leger straw varieties at the temperature of 700°C were 7.2, 5.3, and 4.3%, respectively.

Table 3
Thermal Degradation in the First Reaction Zone

Type of straw	Water evolved, %	Initial degradation temperature, °C	Final temperature, °C	Total degradation, %	Average degradation rate, %/min	Maximum degradation rate, %/min
Kadeth	7.9	186	330	46.5	6.5	22.9
Laurier	7.1	229	377	58.1	7.9	19.6
Leger	9.3	223	385	62.6	7.7	24.5

Table 4
Thermal Degradation in the Second Reaction Zone

Type of straw	Initial temperature, °C	Final temperature, °C	Total degradation, %	Average degradation rate, %/min	Maximum degradation rate, %/min	Residual weight at 700°C, %
Kadeth	330	498	38.4	4.6	10.0	7.2
Laurier	377	539	29.5	3.6	4.3	5.3
Leger	385	513	23.8	3.7	5.2	4.3

These values compare well to the ash compositions (ASTM D-1102-84) of the straw varieties given in Table 1 (7.41, 4.02, and 3.97% for the Kadeth, Laurier, and Leger straw varieties, respectively).

Kinetic Parameters

Because of the two-step nature of thermal decomposition reactions, it was necessary to determine and use different kinetic parameters to describe the thermal degradation over the entire temperature range with higher accuracy. Therefore the kinetic parameters (activation energy, pre-exponential factor, and order of reaction) of the straw varieties Kadeth, Laurier, and Leger were determined for the first and second reactions zones separately by applying the multiple linear regression method to the thermogravimetric data. The kinetic parameters obtained for the two reaction zones are given in Table 5. They were also presented as Arrhenius Plot in Fig. 4.

The results of the kinetic parameters of the first reaction zone had 96.7–99.6% confidence. A relatively higher activation energy value was obtained for the straw variety Kadeth (103.2 kJ/mol) as compared to those of the straw varieties Laurier (89.1 kJ/mol) and Leger (85.4 kJ/mol). The activation energy values of these two variety of barley straw (Laurier and Leger) compared well to those determined by Ergüdenler and Ghaly (*13*) for the three varieties of wheat straw (Absolvant, Monopol, and Vuka). Although, high activation energy values (130–250 kJ/mol) were reported in the literature for cellulose and lignin components (*20–22*), those reported for wheat and rice straw (*13,15,18*) were in the range of 69–130 kJ/mol for the active zone.

The results of the kinetic parameters of the second reaction zone had 75.2, 93.1, and 98.7% confidence for the straw varieties Kadeth, Leger, and Laurier, respectively. The activation energy values obtained for the second reaction zone were lower than those obtained for the first reaction zone. A higher activation energy value was obtained in the second reaction zone for the straw variety Kadeth (58.6 kJ/mol) as compared to those obtained for the straw varieties Laurier (34.8 kJ/mol) and Leger (37.9 kJ/mol). The activation energy values obtained for the second reaction zone for the straw varieties Laurier and Leger compared well to those determined by Ergüdenler and Ghaly (*13*) for three varieties of wheat straw (Absolvant, Monopol, and Vuka).

The order of reactions determined for the first reaction zone were in the range of 2.0–2.3, the largest value corresponding to the straw variety Laurier and the lowest value corresponding to the straw variety Leger. However, much lower (1.1–1.2) orders of reaction were obtained for the second reaction zone for all straw varieties. In most kinetic studies researchers assumed first-order reactions (*15,18,21,22,24*). Ergüdenler and Ghaly (*13*) and Duvvuri et al. (*23*) reported order of reaction values in the range of 1.1–2.0 for wheat straw and 1.2–1.4 for cellulose, respectively.

Table 5
Kinetic Parameters

Type of straw	First reaction zone				Second reaction zone			
	TR, °C	*A*, min^{-1}	*E*, kJ/mol	*n*, -	*TR*, °C	*A*, min^{-1}	*E*, kJ/mol	*n*, -
Kadeth	186–330	49.10×10^7	103.2	2.0	330–498	14.43×10^2	58.6	1.2
Laurier	229–377	1.79×10^7	89.1	2.3	377–539	0.17×10^2	34.8	1.2
Leger	223–385	0.73×10^7	85.4	2.0	385–513	0.27×10^2	37.9	1.1

TR = Temperature range
A = Pre-exponential factor.
E = Energy of activation.
b = Order of reaction.

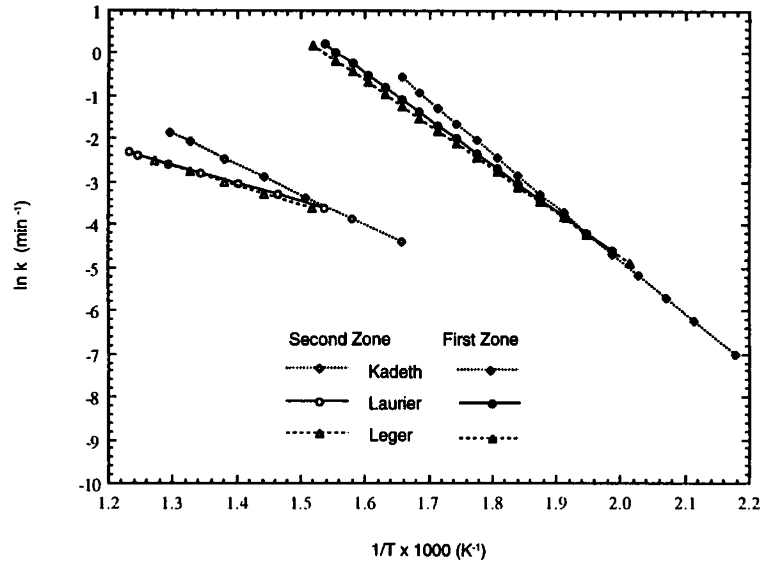

Fig. 4. The kinetic parameters of the straw varieties Kadeth, Laurier, and Leger determined for the two reaction zones presented as Arrhenius plot.

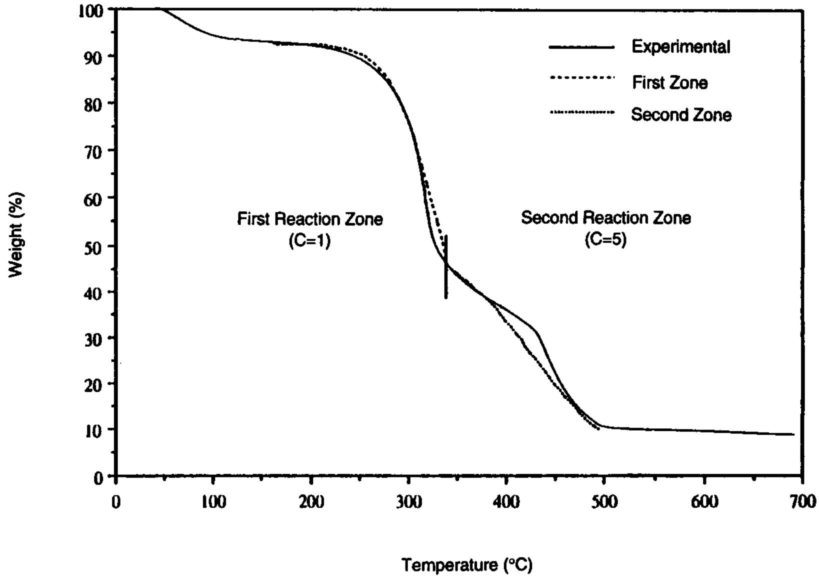

Fig. 5. The predicted and the experimental thermogravimetric curves for the Kadeth variety of barley straw.

The thermal degradation of each variety of barley straw was predicted numerically using the kinetic parameters given in Table 5 in the rate equation (Eq. [1]). The predicted results were compared with the experimental data as shown in Figs. 5–7. The predicted and the experimental thermogravimetric curves were in good agreement for all straw varieties until the

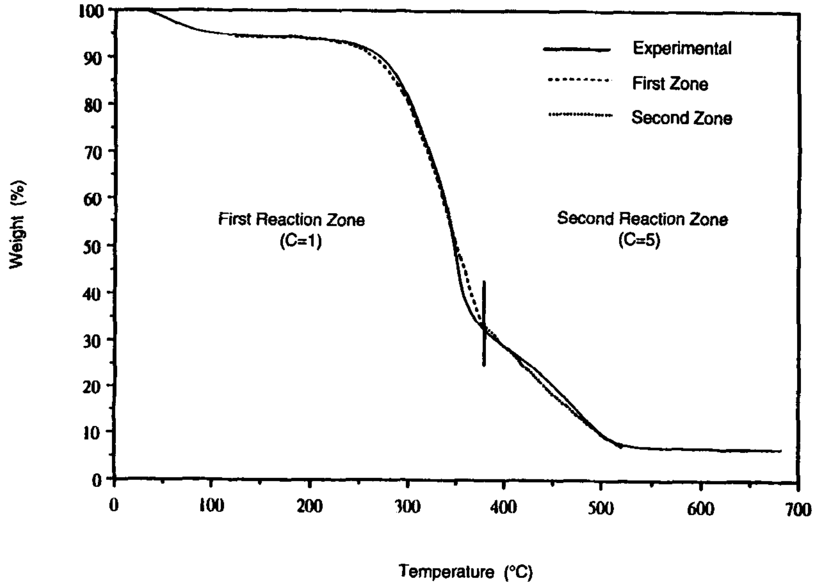

Fig. 6. The predicted and the experimental thermogravimetric curves for the Laurier variety of barley straw.

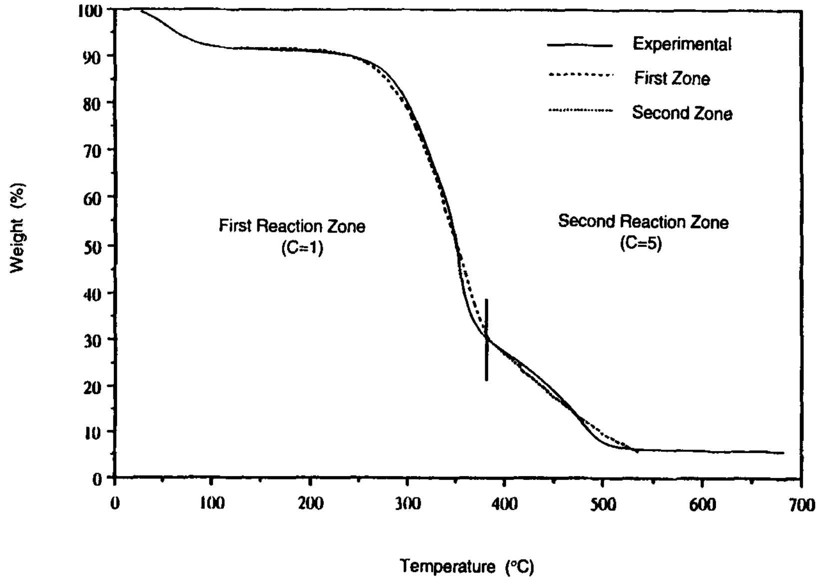

Fig. 7. The predicted and the experimental thermogravimetric curves for the Leger variety of barley straw.

end of the first reaction zone. When the estimated parameters of the first reaction zone were used in the second reaction zone, the thermal degradation was over predicted. On the other hand, when the estimated parameters for the second reaction zone were used, the thermal degradation in second zone was under-predicted.

However, it was possible to improve the predictions in the second reaction zone by modifying the pre-exponential factor in Eq. (3). In this study, the thermal degradation of barley straw can be predicted with high accuracy if the proper values of the factor C in Eq. (3) were used for each reaction zone (1 for the first reaction zone and 5 for the second reaction zone). In their studies on four varieties of wheat straw, Ergüdenler and Ghaly (*13*) reported values of 1 and 5 for the factor C for the first and the second reaction zones, respectively.

However, some discrepancies between the predicted and the experimental thermogravimetric curves were observed for the Kadeth variety in the second reaction zone. Instead of two partially overlapping reactions (which was observed for the Laurier and Leger varieties), two separate exothermic reactions took place for the Kadeth variety. This resulted in a drastic change in the slope of the TG curve in the middle of the second reaction zone at the temperature of 435°C, which corresponded to the temperature at which differential temperature of the second exothermic reaction reached its peak value.

CONCLUSIONS

Two distinct reaction zones were observed both on the TGA and DTA curves. At the beginning of the thermal degradation process the water content (7.1, 7.9, and 9.3% for the straw varieties Laurier, Kadeth, and Leger, respectively) of the straw was evaporated. This was followed by a rapid devolatilization in the first reaction zone and relatively slower char reactions in the second zone. The DTA curves of the Laurier and Leger varieties showed that two partially overlapping exothermic reactions took place between 250 and 550°C. However, two separate exothermic reaction peaks were obtained for the Kadeth variety. For all varieties of barley straw, the average thermal degradation rates were significantly higher for the first reaction zone (6.5–7.9%/min) than those of the second reaction zone (3.6–4.6%/min). The residual weights observed at 700°C were 4.3, 5.3, and 7.2% for the straw varieties Leger, Laurier, and Kadeth, respectively.

It was essential to determine the kinetic parameters for the two reaction zones separately, in order to represent the thermal degradation with higher accuracy for the entire temperature range. The activation energy values and the order of reactions were significantly lower for the second reaction zone as compared to those of the first reaction zone for all barley straw varieties. Higher activation energy values were obtained for the straw variety Kadeth both in the first and second reaction zones as compared to the straw varieties Laurier and Leger. The predicted thermal degradations were in good agreement with the experimental data in the first reaction zone. However, it was necessary to multiply the pre-exponential factors obtained for the second zone by a factor of 5 in order to improve the prediction of thermal degradations in this zone.

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