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Determination of Reaction Kinetics of Wheat Straw Using Thermogravimetric Analysis

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ABSTRACT

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have been conducted on straws from four different wheat varieties (Absolvant, Max, Monopol, and Vuka) in an oxidizing atmosphere of 15% oxygen and 85% nitrogen. The thermal degradation of wheat straw was studied from ambient temperature to 700°C using a heating rate of 20°C/min. By applying thermoanalytical techniques to reaction kinetics, the order of reaction, preexponential factor, and energy of activation were determined from thermogravimetric curves. Two distinct reaction zones were observed on the TGA and DTA curves. Because of the two-step nature of the thermal degradation of wheat straw, it was essential to determine the kinetic parameters for each zone separately. The thermal degradation rate of the first zone was significantly higher than that of the second zone for all wheat straw varieties. Lower activation energy and preexponential factors were observed for wheat straws as compared to cellulose owing to the high inorganic material and silica contents of the wheat straw.

Index Entries: TGA; wheat straw; oxidizing atmosphere; kinetics; activation energy.

INTRODUCTION

Straw, as an agricultural residue, is one of the most abundant and geographically well distributed biomasses. The worldwide estimated annual straw production is about 2340 million tons (*1*). Wheat crop alone

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yields over 750 million tons of straw, of which 60–80% can be made available for energy recovery through combustion and/or gasification processes (*2*). However, the development of technically and economically feasible systems for the conversion of straw to energy by thermal processes requires a fundamental understanding of the complex transitions involved. Although, numerous feasibility studies have been conducted to assess the potential of crop residues, especially cereal straw, for energy recovery through thermochemical conversion processes (*3–5*), many of these projects could achieve only limited success, mainly because of the lack of adequate information on the straw properties pertaining to thermochemical conversion processes (*6,7*).

Cellulose, hemicellulose, and lignin are the major components of straw. Cellulose is a pure organic substance. Hemicellulose acts as the cement material holding together the cellulose micelles and fibers (*8*). The functions of lignins, which are polymers of aromatic compounds, are to: provide structural strength, provide sealing of the water-conducting system, and protect plants against degradation (*9*). These compounds, however, exhibit different thermal behaviors. At moderate heating rates, the thermal degradation of cellulose starts at 300°C and proceeds at higher rates, leaving 5 to 15% residue depending on the size and source of cellulose (*10,11*). Hemicellulose is the least stable component of biomass. It starts decomposing at lower temperatures than cellulose (*11*). Thermal decomposition of lignin starts at lower temperatures than cellulose, but it decomposes at a lower rate than cellulose and hemicellulose, leaving a higher percentage of residue (*12*). Although different components of straw exhibit different thermal behaviors, the overall thermal behavior of the aggregate reflects the sum of the thermal behaviors of its components (*13–16*).

Thermogravimetric analysis techniques have been used to study the thermal behavior of different types of biomass. Although, cellulose, one of the major constituents of straw, has been extensively investigated for its thermal behavior, straw itself has not been given the same consideration (*17,18*). Results reported on dynamic thermal analysis of straw (*17–20*) showed that thermal behavior of straw did not differ much from one kind to another. Thermogravimetric analysis carried on different types of straw by Ghaly and Ergudenler (*18*) at three different heating rates, both in air and nitrogen atmospheres, showed that at lower temperatures higher rates of thermal degradation were obtained in the presence of oxygen-than in the absence of oxygen. Also, less residual weights were recorded at 600°C in the air atmosphere compared to that of nitrogen atmosphere. However, the chemical composition, heating rate, ambient temperature, and inorganic substances are the major factors affecting the thermal behavior of biomass (*7,16–18*).

Thermogravimetry is one of the most widely used methods to study the kinetics of thermal decomposition reactions (*13,19,21–23*). Many investigators assumed that the reactions following the Arrhenius kinetics are first order (*19,22,24*). According to Agrawal (*24*), when cellulose is heated, it decomposes via two competitive first-order reactions to the gaseous products and residual chars. In the kinetic model proposed by Koufopanos et al. (*14*) for the pyrolysis of the main biomass component (cellulose, hemicellulose, and lignin), the order of reaction was taken as 0 for the first reaction and 1.5 for the second and the third reactions. The order of reaction determined by Duvvuri et al. (*13*) for cellulose varied between 1.2–1.4, depending on the heating rate. The values of the activation energy reported in the literature vary from 40–250 kJ/mol and the preexponential factor varied from 10^4 to over 10^{20} s^{-1}. The large variation in the reported values was owing to differences in the methods and heating rates used, and also differences in the chemical compositions (*14*).

THEORETICAL BACKGROUND

Thermogravimetric analysis is one of the major thermal analysis techniques used to study the thermal behavior of carbonaceous materials. It offers a semi-quantitative understanding of the thermal degradation process under well-controlled laboratory conditions (*25*). The advantages of determining the kinetic parameters from TGA curves are that only a single sample and considerably fewer data are required for calculating the kinetics over an entire temperature range in a continuous manner. Equations based on the classical kinetic theory and TGA data were extensively used for engineering predictions. Calculation of kinetic parameters from TGA data was based on the following rate expression (*26*):

$$(dX/dt) = -\mathrm{k}X^n \tag{1}$$

where X is the weight of sample undergoing reaction (kg), n is the order of reaction, k is the specific rate constant (min^{-1}), and t is the time (min).

It was assumed that the rate constant (k) changes with absolute temperature according to the following Arrhenius equation:

$$\mathrm{k} = A\,e^{-E/RT} \tag{2}$$

where A is the preexponential factor (min^{-1}), E is the energy of activation (cal mol^{-1}), R is the universal gas constant (1.987 cal mol^{-1}–$°\text{K}^{-1}$), and T is the absolute temperature (°K).

The technique, which was based on the Arrhenius equation of the form presented by Goldfarb et al. (*27*) and proposed by Duvvuri et al. (*13*), was used to determine the kinetic parameters from typical graph of the thermogravimetric data over an entire temperature range in a continuous manner without any missing regions. Taking the logarithms, the Arrhenius equation was presented in linearized form as follows:

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

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).

The above equation can be written in a simplified form as follows:

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

where: $y = \ln\{[-1/(w_o - w_f)]\,(dw/dt)\}$, $x = 1/(RT)$, $z = \ln[(w - w_f)/(w_o - w_f)]$, $B = \ln A$, $C = -E$, and $D = n$. Using the least-square technique, the values of A, $-E$, and n can be determined from the data obtained from the TGA curves.

OBJECTIVES

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

a. To conduct thermogravimetric and differential thermal analyses on four types of wheat straws (Absolvant, Max, Monopol, and Vuka) at the heating rate of 20°C/min in an oxidizing atmosphere of 15% oxygen and 85% nitrogen;
b. To determine the thermal degradation rate in the first and the second reaction zones, the initial degradation temperature, and the residual weight at 700°C; and
c. To determine the kinetic parameters (the order of reaction, the preexponential factor, and the energy of activation) using thermogravimetric curves.

EXPERIMENTAL PROCEDURE

Straw Collection

Four major types of wheat were selected for the thermogravimetric and differential thermal analyses. The selected varieties were: Absolvant, Max, Monopol, and Vuka. Straw samples were obtained from harvested fields in the Annapolis Valley, 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 resulting from moisture content. The dried straws were stored in polyethylene bags for future processing.

Sample Preparation

Dried straw samples of 1 kg each were first coarse ground through a 20-mesh sieve on a medium-size Wiley Mill. 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 homogeneous samples. These were stored in air-tight plastic containers until they were needed for the thermogravimetric analysis. This procedure ensured reproducible thermogravimetric results.

Thermal Analysis

Straw samples were subjected to thermogravimetric (TGA) and differential thermal (DTA) analyses 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 analysis. 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 that 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 size is recommended. 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 the microbalance, which has a precision of $\pm 0.1\ \mu g$. The base with the furnace was controlled by the TA Processor. The furnace temperature in the TG50 Thermobalance was controlled in such a way that the sample temperature followed the desired profile. For this purpose, the temperature equilibration function between the furnace and the sample was provided by the manufacturer (Mettler Instrument AG). 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, which 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 $\pm 2°C$. For a higher temperature homogeneity in the sample, platinum crucibles with a volume of 0.07 mL were used.

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

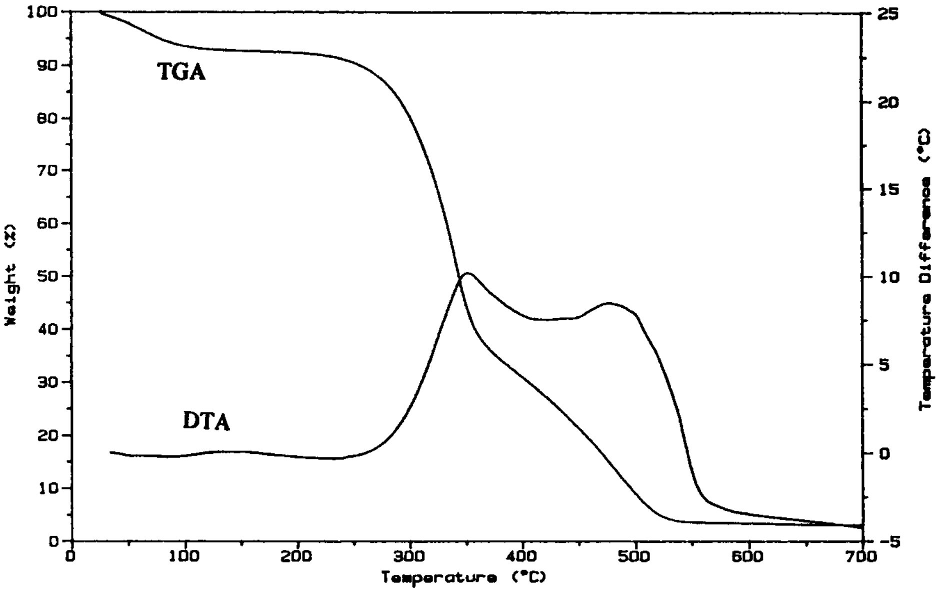

Fig. 1. Thermogravimetric and differential thermal analyses of Absolvant wheat straw in an oxidizing atmosphere. Sample: Absolvant, size: 13.6870 mg, heating rate: 20°C/min, atmosphere: 15% oxygen, 85% nitrogen.

RESULTS AND DISCUSSION

The results obtained by dynamic thermal analyses (TGA and DTA) for different varieties of wheat straw are shown in Figs. 1–4. It is evident from both the TGA and DTA curves that two overlapping reactions took place between 250–550°C for all straw varieties.

Thermogravimetric Analysis

Initial weight losses of 6.4–7.8% were observed on the TGA curves and also showed as small endotherms on the DTA curves at around 75°C. These small weight losses were the result of the evolution of water from the samples. Approximately 7.8, 6.8, 6.4, and 7.6% of weight losses (owing to water evolution) were observed with Absolvant, Max, Monopol, and Vuka straw varieties, respectively. This was followed by a period of relatively constant weight.

The initial decomposition of straw samples (at the heating rate of 20°C/min) started at a temperature between 205–222°C depending on the variety of straw (Table 1). The observed initial deformation temperatures for Absolvant, Max, Monopol, and Vuka straw varieties were 222, 205, 210, and 215°C, respectively. The difference in these temperatures is most likely the result of the differences in the cellulose, hemicellulose, and

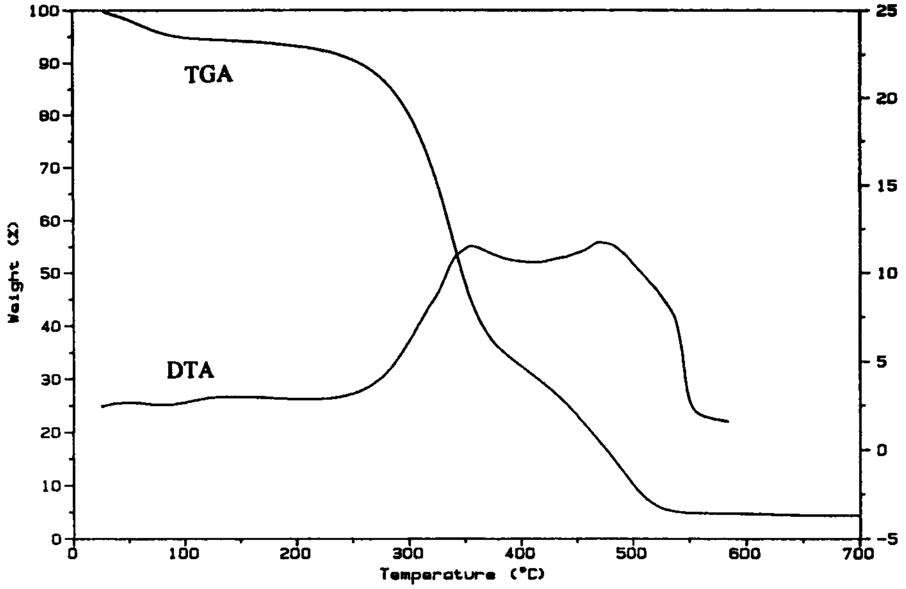

Fig. 2. Thermogravimetric and differential thermal analyses of Max wheat straw in an oxidizing atmosphere. Sample: Max, size: 10.3080 mg, heating rate: 20°C/min, atmosphere: 15% oxygen, 85% nitrogen.

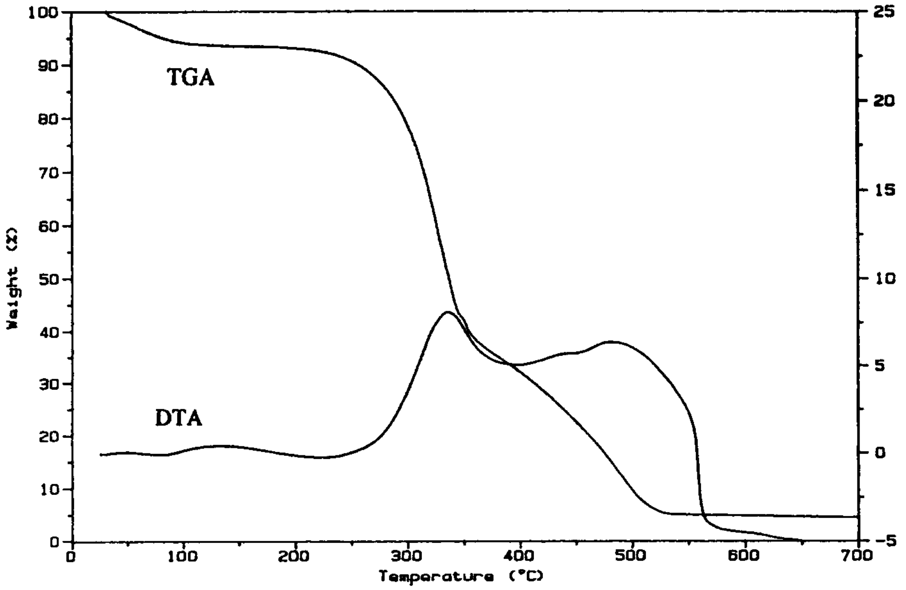

Fig. 3. Thermogravimetric and differential thermal analyses of Monopol wheat straw in an oxidizing atmosphere. Sample: Monopol, size: 12.0300 mg, heating rate: 20°C/min, atmosphere: 15% oxygen, 85% nitrogen.

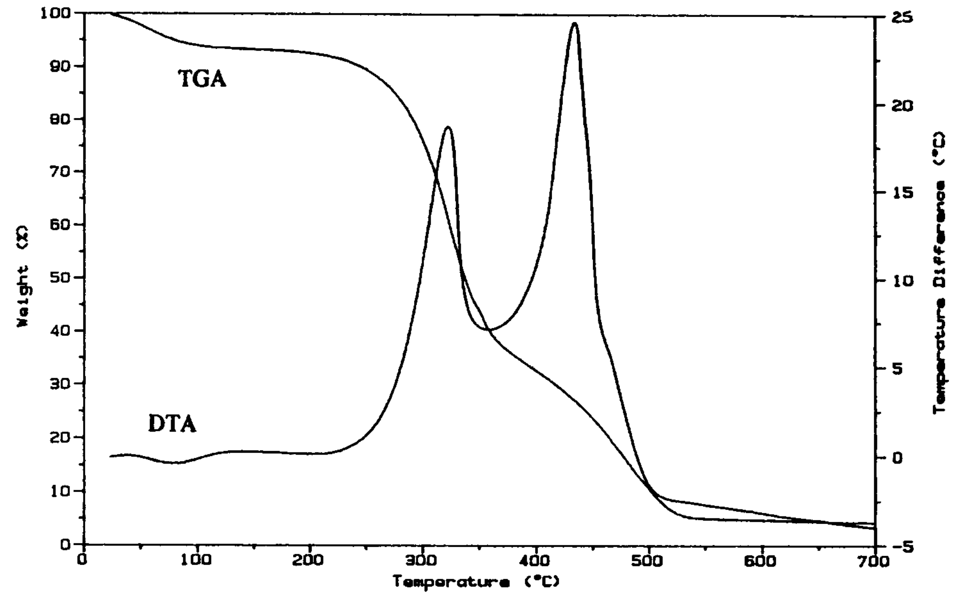

Fig. 4. Thermogravimetric and differential thermal analyses of Vuka wheat straw in an oxidizing atmosphere. Sample: Vuka, size: 11.1000 mg, heating rate: 20°C/min, atmosphere: 15% oxygen, 85% nitrogen.

Table 1
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
Absolvant	7.8	222	363	54.0	7.7	19.1
Max	6.8	205	373	55.4	6.6	15.2
Monopol	6.4	210	350	51.1	7.3	17.1
Vuka	7.6	215	365	53.4	7.1	16.0

lignin contents among the straw varieties. Since the initial deformation temperatures of hemicellulose and lignin are lower than that of cellulose (*9–11*), Absolvant probably has the highest percentage of cellulose, and Max has the lowest cellulose content.

Slightly above the initial deformation temperature (250 and 350°C), the straw samples decomposed at very high rates. This zone is the first reaction zone and is referred to as the active pyrolysis zone because of the high degradation rates. The average degradation rates in this zone ranged from 6.6%/min (for Max) to 7.7%/min (for Absolvant). The maximum degradation rates observed for Absolvant, Max, Monopol, and Vuka were 19.1%/min, 15.2%/min, 17.1%/min, and 16.0%/min at temperatures of 340, 335, 320, and 325°C, respectively.

Table 2
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 %
Absolvant	363	543	34.4	3.8	5.5	3.0
Max	373	527	32.6	4.2	5.5	4.2
Monopol	350	527	37.4	4.5	5.6	4.5
Vuka	365	538	34.0	4.3	5.6	4.3

Table 3
Proximate Analysis, % Dry Basis

Type of straw	Volatile matter, %	Fixed carbon, %	Ash, %
Absolvant	79.85	17.06	3.09
Max	79.61	16.76	3.63
Monopol	77.80	17.61	3.59
Vuka	77.04	18.15	4.81

A noticeable change in the slope of all TGA curves was observed at around 350–365°C, indicating the initiation of a second reaction zone. The thermal degradation rates were lower in this zone compared to the first reaction zone. Thus, the second zone was referred to as the passive pyrolysis zone. In this zone (350–543°C), the average thermal degradation rates were between 3.8–4.5%/min (Table 2).

However, between temperatures of 543–550°C and 700°C, almost no changes in the weight of the samples were recorded. The residual weights at 700°C for Absolvant, Max, Monopol, and Vuka were 3.0, 4.2, 4.5, and 4.3%, respectively. These values were close to the ash content of the samples (Table 3), which indicates that, at the heating rate of 20°C/min, thermal degradation was completed at above 527–543°C depending on the straw variety.

The total decomposition in the first and second reaction zones was around 55 and 35%, respectively. The decomposition in the first zone can be attributed to the oxidation of volatile products, whereas that in the second zone can be attributed to the oxidation of the residual chars (*17*). However, previous studies of Ghaly et al. (*28*) on proximate analysis of straw showed that the concentration of volatile matter in wheat straws was about 80% (Table 3). This shows that a part of the volatiles continued oxidizing in the second reaction zone together with the residual chars. The two overlapping exothermic peaks on DTA curves are also a good indication of this phenomena.

Table 4
Differential Thermal Analysis

Type of straw	Exothermic peaks				
	First peak		Second peak		
	Temperature, °C	ΔT, °C	Temperature, °C	ΔT, °C	Peak area, °C/min-mg
Absolvant	352	10.0	425	8.4	9.44
Max	360	11.8	473	12.0	8.75
Monopol	332	8.1	477	6.4	8.91
Vuka	324	18.8	438	24.6	10.95

ΔT = temperature difference owing to exothermic reactions.

Differential Thermal Analysis

The DTA curves (Figs. 1-4) showed how exothermic (or endothermic) the reactions were. The two partially overlapping exothermic peaks on DTA curves denote the two-step weight loss on the TGA curves, whereas the small endothermic peaks observed at around 75°C indicate the energy absorbed during the evaporation of the moisture in the samples. Strong exothermic reactions started at around 250°C (which also corresponds to the the beginning of the rapid decomposition on TGA curves) and ended at around 550°C (which corresponds to the temperature at which thermal decomposition ceased). The first exothermic peak, which was the result of the oxidation of the volatile products, occurred at 352, 360, 332, and 324°C for Absolvant, Max, Monopol, and Vuka, respectively (Table 4). The second exothermic peak, which was mostly the result of the oxidation of char, occurred at 425, 473, 477, and 438°C for Absolvant, Max, Monopol, and Vuka, respectively. The temperature difference recorded for the first and second peaks was around 10°C for Absolvant, Max, and Monopol, and the nature of the peaks indicated the two partially overlapped exothermic reactions for these three varieties of straw. In the case of Vuka, two sharp peaks were observed (Fig. 4) at 324 and 438°C with the temperature difference of 18.8 and 24.6°C for the first and second reaction peaks, respectively.

Kinetic Parameters

Thermoanalytical methods (thermogravimetric and differential thermal analyses) have been used widely to study the kinetics of thermal decomposition reactions. Although, a great deal of effort has gone into fitting the classical kinetic theory of TGA data in general, there is no generally accepted method for determining kinetic parameters from the thermogravimetric data. In this study, the technique proposed by Duvvuri et al.

Table 5
Kinetic Parameters

Type of straw	Temperature range, (°C)		A, min^{-1}		E, kJ/mol		*n*, –	
	FRZ	SRZ	FRZ	SRZ	FRZ	SRZ	FRZ	SRZ
Absolvant	222-363	363-543	2.2×10^6	0.18×10^2	80.2	34.0	1.34	1.22
Max	205-373	373-527	2.0×10^5	0.32×10^2	69.3	37.6	1.21	1.18
Monopol	210-350	350-527	2.4×10^6	0.24×10^2	80.4	36.2	1.25	1.16
Vuka	215-365	365-538	5.4×10^6	0.35×10^2	81.3	39.6	1.96	1.07

FRZ = first reaction zone.
SRZ = second reaction zone.
A = preexponential factor.
E = energy of activation.
n = order of reaction.

(*13*), which was based on Goldfarb et al. method (*27*), was used to determine the kinetic parameters of wheat straw samples from thermogravimetric analysis. The coefficients B, C, and D in Eq. 4, which correspond to the logarithm of preexponential factor (1n A), the energy of activation (E), and the order of reaction (*n*), respectively, were determined for each type of straw by the multiple linear regression analysis method.

It was evident both from TGA and DTA curves (Figs. 1-4) that two distinct reaction zones existed during the thermal degradation of wheat straws in the oxidizing atmosphere. Because of the two-step nature of decomposition, it was not possible to use the same kinetic parameters to describe the thermal degradation over the entire temperature range accurately. Therefore, it was decided to determine the kinetic parameters for each reaction zone separately. Some investigators (*19,23,29*) have reported dual activation energies for cellulose over different temperatures based on dynamic TG studies. Others (*24,26*) found it difficult to justify the derivation of dual activation energies based on a single smooth curve, such as the TGA curve of cellulose. In this study, derivation of dual activation energies for wheat straw was essential, since the TGA data exhibited dual curve characteristics rather than a single smooth curve. Thermogravimetric curves of wheat straw did not follow the usual trend that applies to pure cellulose or any other single component. There was a different trend between 350–550°C, which required different values for the kinetic parameters in order to represent the thermal degradation in the second zone with higher accuracy.

The results of the kinetic parameters were obtained for the first and second reaction zones by multiple regression analysis as given in Table 5. The results obtained for the kinetic parameters of the first reaction zone had 99.5% confidence. Within the temperature range of 250–350°C (first reaction zone), the kinetic parameters were in agreement with the TGA data.

Table 6
Major Mineral Elements Composition of Straw Ash, % by Weight

Type of straw	Si	K	Ca	P	Mg
Absolvant	14.99	21.11	10.76	4.21	3.15
Max	19.20	19.18	8.09	2.60	3.24
Monopol	12.98	30.00	7.71	2.84	2.53
Vuka	12.72	42.35	6.02	2.40	1.85

Table 7
Major Mineral Oxides Composition of Straw Ash, % by Weight

Type of straw	SiO_2	K_2O	CaO	P_2O_5	MgO
Absolvant	31.47	25.43	15.05	9.65	5.22
Max	40.37	23.87	11.32	5.95	5.37
Monopol	27.26	36.15	10.79	6.50	4.19
Vuka	26.71	51.03	8.43	5.50	3.07

The activation energy values determined in the first reaction zone were very close for the varieties of Absolvant, Monopol, and Vuka (80.2, 80.4, and 81.3 kJ/mol, respectively), whereas for the Max variety the activation energy was lower (69.3 kJ/mol). Kinetic studies done on rice straw by Nassar (*19*), revealed very comparable results for the activation energy to those obtained in this study. Although, the determined activation energy values are in good agreement with those reported by Koufopanos et al. (*14*) for hemicellulose component, they are significantly lower than the activation energy values reported by Duvvuri et al. (*13*), Koufopanos et al. (*14*) and Agrawal (*24*) for cellulose and lignin components. Nassar (*19*) explained the low activation energy for nonwood plants by high silica content. The lower activation energy obtained in this study for the Max variety can also be explained as resulting from the relatively higher silica content of this variety as compared to the others (Tables 6 and 7). Previous studies (*20,29,30*) also support the finding that impurities (or addition of inorganic materials) have an effect on the kinetic reaction of lignocellulosic materials. Preexponential factors determined for the wheat straw were also low compared to those obtained for cellulose or lignin components.

The results obtained for the kinetic parameters of the second reaction zone had 93–97% confidence. The activation energy values determined in this zone were 34.0, 37.6, 36.2, and 39.6 kJ/mol for Absolvant, Max, Monopol, and Vuka, respectively. Previous studies done on different biomass components (*8–10*) showed that cellulose and hemicellulose decompose at higher rates than lignin leaving 5–15% residues at around 300–350°C.

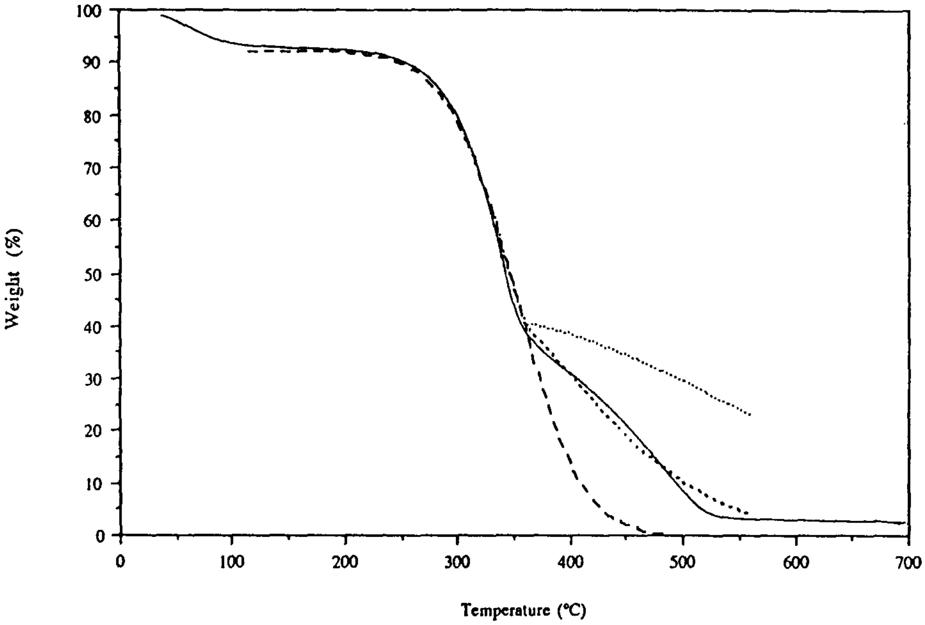

Fig. 5. The experimental and the predicted thermogravimetry curves of the Absolvant wheat straw. —— Experimental, ---- first zone, ... second zone (C=1), •••• second zone (C=5).

The lignin component was mainly condensed to char, giving smaller amounts of pyrolyzates that mostly decomposed at temperatures over 350°C since higher temperatures are required to convert char. It was also shown that the natural impurities and ash content lowered pyrolysis rate and increased char formation (*16,30*). It is most likely that this resulted in lower activation energy values in the second reaction zone.

In the previous studies, the reaction was assumed to be the first order by many researchers (*14,19,22,24*). In this study, the order of reaction was determined by multiple linear regression analysis technique. The order of reaction was around 1.3 in the first reaction zone, and 1.2 in the second reaction zone for the varieties of Absolvant, Max, and Monopol. The order of reaction for the variety of Vuka was determined as 2.0 in the first zone and as 1.1 in the second zone.

The values of the kinetic parameters (A, E, and n) obtained from the thermogravimetric curves were used in the rate equation (Eq. 1) to predict the thermal degradation of straw. The rate expression is given below in a more explicit form:

$$(dX / dt) = - A e^{-E/RT} X^n \tag{5}$$

This was integrated numerically using Fourth-order Runge-Kutta method with Predictor-Corrector method (*31*). The theoretical results were plotted to compare the predicted values with the experimental results. The plots of the experimental and predicted TG curves are shown in Figs. 5–8. As shown in these figures, if the values of the kinetic parameters obtained

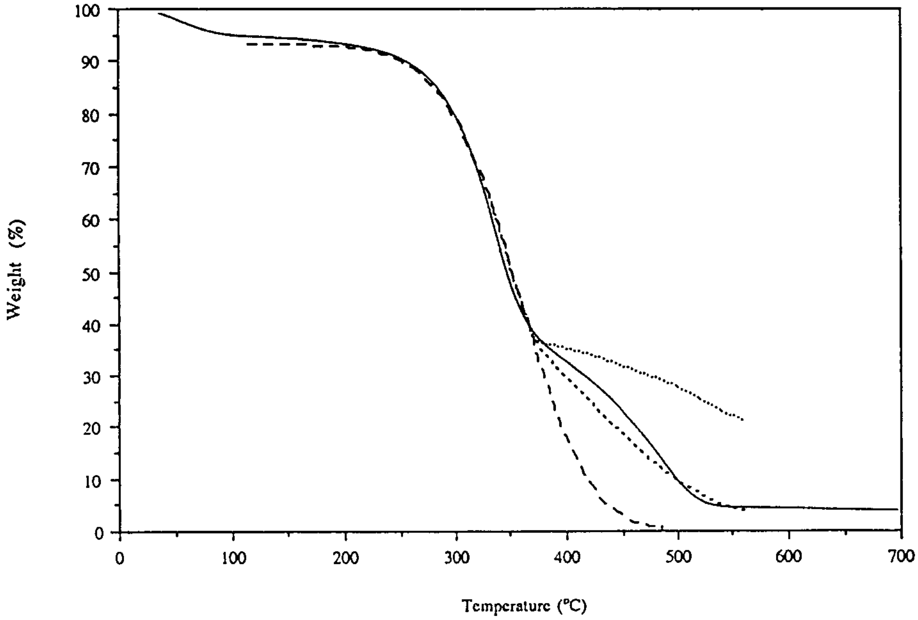

Fig. 6. The experimental and the predicted thermogravimetry curves of the Max wheat straw. —— Experimental, ---- first zone, ... second zone (C=1), •••• second zone (C=5).

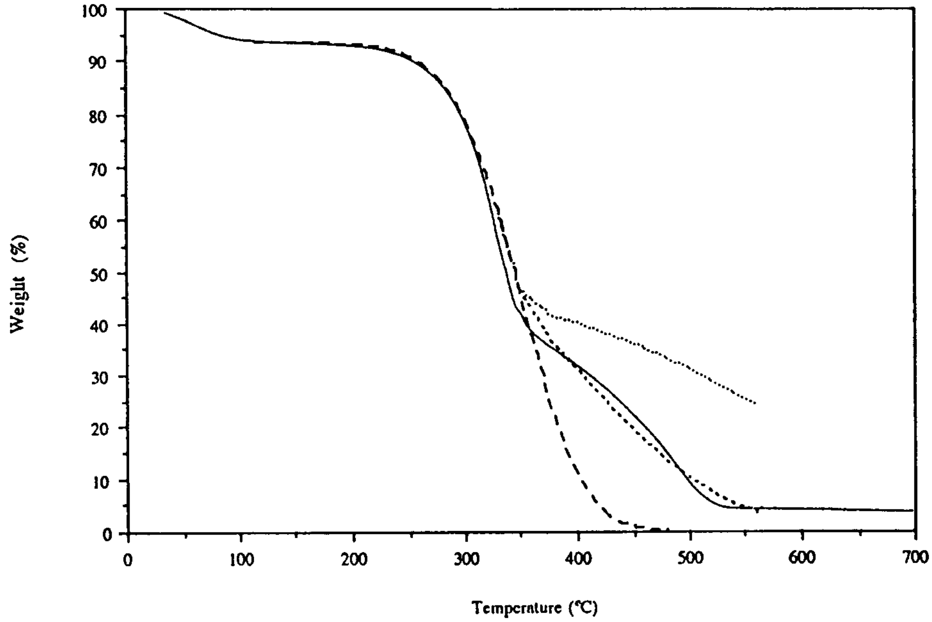

Fig. 7. The experimental and the predicted thermogravimetry curves of the Monopol wheat straw. —— Experimental, ---- first zone, ... second zone (C=1), •••• second zone (C=5).

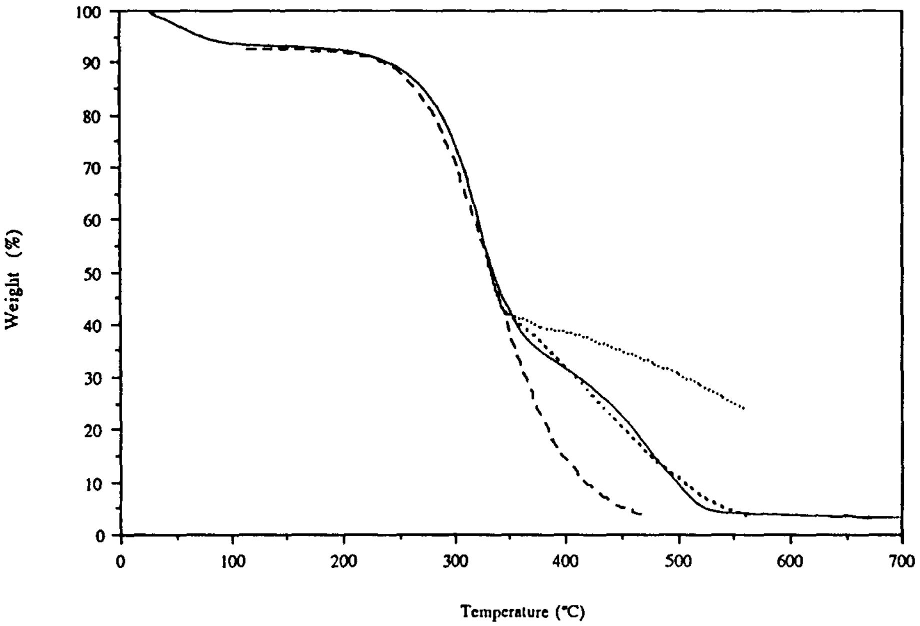

Fig. 8. The experimental and the predicted thermogravimetry curves of the Vuka wheat straw. —— Experimental, ---- first zone, ... second zone (C = 1), •••• second zone (C = 5).

for the first zone are used for the entire degradation process, the total degradation for the second zone (above 350°C) would be overestimated. On the other hand, when the parameters determined for the second reaction zone (350–550°C) were used to predict the thermal degradation over 350°C, the thermal degradation was underestimated in this region. This was because of the change in the usual exponential trend of thermal degradation at temperatures over 350°C.

Therefore, it was essential to correct the preexponential factor (A) in Eq. 5, and thus, the rate expression was modified as follows:

$$(\mathrm{d}X / \mathrm{d}t) = -C A e^{-E/RT} X^n \quad (6)$$

Equation 6 can be used to predict the thermal degradation rate of different straw varieties with high accuracy for the entire temperature range when the proper values of the factor C and the kinetic parameters for two different zones were used. The factor C was found to be one for the first zone and five for the second zone for all wheat straw varieties.

CONCLUSIONS

Two distinct reaction zones were observed on the TGA curves. DTA curves also showed that two partially overlapped exothermic reactions took place between 250–550°C. The thermal degradation rates in the first reaction zone were significantly higher than those in the second reaction zone. Because of the two-step nature of the thermal degradation of wheat straw shown in TGA, it was essential to determine the kinetic parameters for each zone separately, in order to represent the thermal degradation with higher accuracy for the entire temperature range. The activation energies, determined for all varieties of wheat straw in the first reaction zone, were in good agreement, except that for the Max variety, which had a lower activation energy. The low activation energies and preexponential factors of wheat straw as compared to cellulose were owing to its high content of inorganic materials, such as silica. Total thermal degradation was overestimated between the temperatures of 350–550°C if the kinetic parameters of the first zone were used over the entire temperature range. Total thermal degradation of wheat straw can be predicted with higher accuracy if the kinetic parameters of the second reaction zone were modified by multiplying the preexponential factors by a factor of five.

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