Kinetic Study of Cotton Stalk and Rice Husk Samples under an Inert and Oxy Combustion Atmospheres

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ABSTRACT

Biomass materials such as CS (Cotton Stalks) and RH (Rice Husk) are a renewable source of energy. As biomass resources have potential to offer a uninterpted supply of biofuels through thermal decomposition processes. Nevertheless, an appropriate understanding of reaction kinetics and thermal properties of biomasses play a vital role in designing of the commercial plants using biomass as a raw material for energy generation. The kinetic characteristics of the CS and RH samples under pure nitrogen 99.9% and pure oxygen 99.9% was performed. The temperature was raised from ambient to 900ºC maintaining the heating rate of 10ºC/min. CS and RH decomposition was noticed in three dissimilar regions. The kinetic characteristics such as (pre-exponential factor, the order of reaction and activation energy) were calculated for both selected materials. The activation energies calculated under nitrogen environment for CS and RH was 68.77 and 72.31 kJ/mole, whereas the regression coefficient (R^2) was 0.9877 and 0.9731 respectively. The activation energies under oxygen environment were higher, it was 106 and 118 kJ/mole. The regression coefficient (R^2) under oxygen environment was 0.9987 and 0.99883 for above sample sequence.

Key Words: Rice Husk, Cotton stalks, Oxygen, Thermogrammetric Analysis, Kinetic Study

1. INTRODUCTION

Fossil fuels consumption and their ever growing demand cause the increase in GHG (Greenhouse Gas) emissions [1]. The application of biomass for clean and sustainable energy in substantial quantities from agricultural residues is considered as one of the best substitute for fossil fuels worldwide. In addition, fossil fuel deposits take millions of years to accumulate, whereas, these deposits are extracted rapidly. Given that the extraction rate of fossil fuels is higher than their replenishment rate, therefore these finite resources will end up in near future [2-3]. Due to rapid depletion of fossil fuels, various governments have planned to alter their energy matrix in order to increase the share of renewable sources [4]. Owing to this fact, researchers and policy

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makers aim to get energy from biomass including agricultural wastes. Agricultural residues include CS, RH, corn straw, wheat straw, and wheat husks, among these sources, CS and RH are least used resources in developing countries [5-8]. Agricultural residues such as CS, RH corn cobs, sugarcane bagasse and wheat straw are a viable source for bioenergy production. The copious quantities of agricultural wastes are underutilized resources in developing countries. These resources of renewable energy are used either as an animal feed or as a raw material for paper industry. The excessive agricultural residues are burned in the fields or left untouched as a waste material, thereby causing substantial environmental hazards. The conversion methods for biomass may be physical, chemical, biological or thermal to give a solid liquid or gaseous products. Among all conversion methods, the thermochemical conversion method seems to be one of the most promising conversion methods for bioenergy production.

Nevertheless, the development of economically and technically viable method for the conversion of the CS and RH residues into higher value fuels through thermochemical conversion processes involves an understanding of its thermal characteristics and reaction kinetics. The thermochemical conversion of agricultural residues is strongly influenced by their chemical composition such as cellulose, hemicellulose and lignin contents [9]. The above agricultural residues can be used to generate energy through direct combustion, which is a less efficient method of energy recovery from residues. The most efficient method to obtain energy from biomass residues is pyrolysis, as through pyrolysis process various energy products such as solid, liquid and gaseous are obtained. Hence for valid kinetic data regarding the thermochemical conversion of RH and CS, it is important to perform comprehensive TGA (Thermogravimetric Analysis) investigation on both selected materials. Therefore, in the present study, TGA techniques were applied to investigate the thermal degradation behavior and kinetic characteristics of RH and CS residues in aninert (N_2) and oxidative (O_2) atmospheres.

This analysis was carried out in order to understand the thermal degradation parameters and reaction kinetics of CS and RH samples. The aims of this study include:

To perform TGAon the CS and RH samples at the heating rates of 10°C/min in an inert (N_2) and oxidative (O_2) environments.

To determine the initial degradation temperatures, thermal degradation rates and residual weight of RH and CS samples at 900°C.

To estimate the kinetic constraints (such as pre-exponential factor, apparent activation energy and order of reaction) by means of TGA data.

2. MATERIALS AND METHOD

The biomasses used in this study included RH and CS from district Khairpur Mirs located in between middle and northern Sindh province, Pakistan. The CS samples were cut into small pieces in order to reduce handling problems. The RH and CS sample were suns dried for 4-5 days in order to reduce the moisture content of selected biomass samples. After drying process the samples were transported to Department of Chemical Engineering, Mehran University of Engineering & Technology, Jamshoro, Pakistan, for size reduction. These samples were ground using a hammer mill, commonly known as beater cross mill. The revolving beater bars of hammer mill reduced the size of samples. These samples were passed through 250 μm (60 mesh). After sieving of RH and CS samples were placed into an airtight plastic bags for TGA. The complete procedure used for the preparation of WAB (Waste Agricultural Biomass) samples include sun drying, hammer milling, sieving and bagging shown in an inverse pyramid in Fig. 1.

2.1 Chemical and Physical Analysis of Waste Agricultural Biomass

Following analysis was done on the CS and RH samples such as TGA, CHNS (Elemental Analyses), density and calorimetric analysis. In order to investigate the chemical properties of WAB regarding the thermochemical conversion, ultimate and proximate investigation were carried out on both biomass materials. Density analysis of WAB was performed using an empty glass cylinder of 100 ml volume. For removal of moisture available in the empty cylinder, the temperature of the oven was maintained at 110°C. The empty cylinder was filled with water up to 100 ml marking. After removal of moisture, a glass cylinder was placed on electronic balance for tare weight. The empty glass was filled with WAB and its mass was determined in grams. The filled volume of water was subtracted from 100 ml that offer a net volume of sample in ml. Results of density analysis are presented in Table 1. For the measurement of calorific value, an adiabatic calorimeter was used. The analysis of bomb calorimeter data was done using formula, which is appropriate for the equipment used. The calorific value of the samples is given in Table 1.

$$HCV = (TD \times 2000 + 585)/Ms$$

TD is a temperature difference of inner cylinder in ^{o}C and Ms is a mass of sample in gram.

2.2 Elemental Analysis of Waste Agricultural Biomass

The analysis of carbon, hydrogen, nitrogen and sulfur elements in WAB was conducted through the standard procedure according to ASTM D3176 method [9]. The percentages of Sulphur, nitrogen, hydrogen and carbon were calculated by using vario MAX elementary analyzer. The percentage of oxygen content was determined by subtracting the percentages of hydrogen, sulphur, nitrogen, carbon and ash from hundred percent. The μμresults of CHNS analysis are given in Table 1.
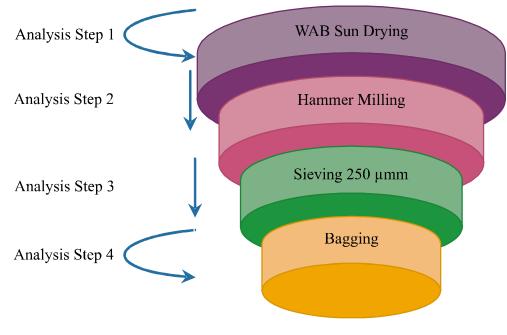

FIG. 1. SYSTEMATIC INVERSE PYRAMID FOR SAMPLE PREPARATION

2.3 TGA of Waste Agricultural Biomass

TGA of WAB materials was determined by using TGA model SDT-Q600 as per ASTM standard method E 1131-08. The TGA analysis has been performed in various previous reports by [10-22]. TGA of agricultural residues and other biomass materials to study the kinetic parameters have been widely used technique [10-22]. In this study, thermal characteristics of the RH and CS samples were checked. The TGA study was conducted at 10°C/min maintaining the nitrogen and oxygen flow rate of 100 ml/h. The temperature was increased from room temperature to 900°C. An experimental study was conducted at slow heating rates in order to comprehend the thermal behavior of selected biomasses. According to this method, WAB samples were taken in the range of 15-30 mg and run in triplicate.

3. RESULTS AND DISCUSSION

3.1 Kinetic Study under (N$_2$) Environment

The thermal behavior of CS and RH samples at a heating rate of 10°C/min under nitrogen environment are presented in Figs. 2-3. The TGA and DTG curves of CS and RH samples elaborate about the mass loss with regard to the temperature and the DTG curves. Certainly, both biomass materials revealed three identical biomass degradation zones during DTG and TGA of samples. In the first zone of TGA and DTG analysis of samples, the mass loss was because of the moisture evaporation followed by hemicellulose, cellulose degradation and in the third and last zone, decomposition was because of the lignin degradation [12]. In the first zone, reduction in mass was because of the moisture evaporation and volatile release observed in thetemperature 22-155°C for cotton stalks and from 24-201°C for RH samples respectively. Whereas the devolatilIzation which is the main pyrolysis stage of mass loss was observed in temperature range from155-449°C for CS and for RH it was observed from 201-560°C, while the third stage of mass loss ranged from temperature from 449-900°C for CS and for RH samples was in temperature range of 560-900°C.

The degradation profiles of CS samples were initiated at a lower temperature when compared with RH degradation profile. Besides, that degradation of CS samples ended at a lower temperature when compared with RH samples.

TABLE 1. THE ULTIMATE AND PROXIMATE ANALYSIS OF RH AND CS

Biomass Type	References	Proximate Analysis			Ultimate Analysis				Bulk Density (kg/m³)	Higher Heating Value (MJ/kg)
		Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)		
RH	This study	65.39	8.96	18.55	34.33	5.36	59.43	0.29	161	15.36
CS	This study	69.98	16.31	8.13	41.73	5.82	52.05	0.10	335	16.81
RH	[23]	61.81	16.95	21.24	38.50	5.20	34.61	0.45	-	14.69
Olive Kernel A	[24]	72.64	24.78	2.58	51.19	6.06	39.32	0.76	-	18.90
Rapeseed	[25]	70	15.8	5.8	41.1	6.0	47.8	5.1	-	19.40
Wheat Straw	[23]	82.12	10.98	6.90	42.95	5.35	46.99	0	-	17.98
Sugarcane Bagasse	[13]	76.1	13.3	5.2	43.79	5.96	43.36	1.69	140	17.7
Sugarcane Bagasse	[23]	83.66	13.15	3.20	45.48	5.96	45.21	0.15	-	18.73
Shea Meal	[13]	61.81	28.7	5.0	48.56	5.86	37.70	2.88	490	19.8

The CS samples revealed higher peak than RH samples under both inert and oxidative atmospheres. The residual weight percent of the CS and RH samples was 13 and 29% respectively.

The DTG curves of both materials RH and CS revealed dissimilar behavior under an inert environment. The DTG curve generated regarding CS degradation profile and RH degradation profile have shown a varying reduction
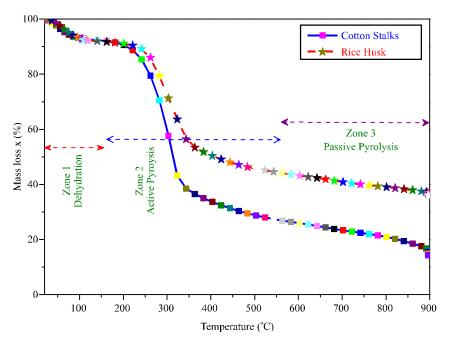

FIG. 2. TGA CURVES OF COTTON STALKS AND RICE HUSK SAMPLES UNDER NITROGEN ENVIRONMENT
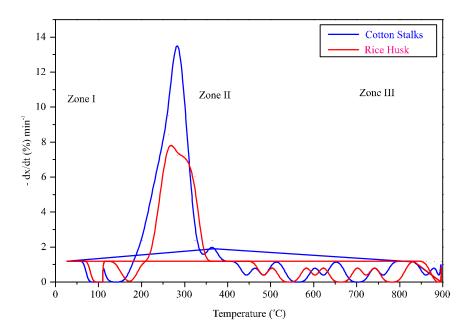

FIG. 3. DTG CURVE OF COTTON STALKS AND RICE HUSK SAMPLES UNDER NITROGEN ENVIRONMENT

trend in mass loss. These dissimilarities in initial decomposition temperatures are due to the difference in elemental and chemical composition biomasses [26]. The main degradation stages of both biomasses ended at 449°C for CS and nearly 560°C for RH samples as shown in Fig. 3. During the pyrolysis of samples, the two different areas of DTG curve were observed. The first region appeared with a more or less prominent shoulder at nearly 197 and 220°C for the sample sequence. Whereas the subsequent second region was followed by the peaks maxima at 260 and 285°C for above sample sequence. The appearance of the shoulder in DTG curve may be due to the degradation of the hemicellulose and lignin. Whereas the generated DTG peak relates to the degradation of cellulose and lignin. However, when cellulose and hemicellulose degradation overlap, at that point the shoulder generated marks the peak of the hemicellulose degradation [11]. Next, to the end of the second degradation stage, a continuous slow degradation of selected biomasses was observed that may correspond to the slow decomposition of lignin. Table 2 summarizes the TGA and DTG curve characteristics. The reactivity RM is directly proportional to the maximum weight loss $RDTG_{max}$ and inversely proportional to the value of its corresponding temperature $TDTG_{max}$. The reactivity of samples was calculated by the method adopted in previous studied performed by [13,17,27].

$$RM = 100\sum \frac{RDTG_{max}}{TDTG_{max}} \qquad (1)$$

RM shows the reactivity (% s^{-1} C-1), $RDTG_{max}$ represents maximum reduction (% s^{-1}) and $TDTG_{max}$ shows peak temperature (°C).

3.2   Kinetic Study under (O_2) Oxygen Environment

TGA curve of RH and CS samples under an oxidative environment at a heating rate of 10°C/min have been drawn against temperature in Figs. 4-5. It is obvious from the data obtained that weight loss occurred in major three stages under oxidative environment. The weight loss of both samples occurred at first stage due to the evaporation of moisture, the weight loss at second stage accounts for devolatilization and the weight loss at third and last stage is due to the combustion of char. The weight loss in the first zone was observed from 23°C to nearly 145°C. At this stage of weight loss, evaporation of water and light molecules may have accounted for weight loss. The weight loss of CS and RH at second stage was observed at temperatures between 153-580°C and at the third stage of weight loss that ranged from 580-900°C was due to the combustion of the sample under oxygen environment. It is estimated that maximum degradation rate occurred at 282 and 365°C for CS and RH samples respectively. At the end of the third stage of weight loss, the residual mass of CS and RH was found 4.3 and 7.4% respectively [26]. Moreover, for those feedstocks producing higher amounts of ash during their combustion, attention must be given to set up the ash removal systems before the setting up of the commercial unit.

TABLE 2. KINETIC BEHAVIOR OF TGA EXPERIMENTS UNDER AN INERT ATMOSPHERE

Sample	Temperature Range (°C)	Rshoulder (% s^{-1})	Tshulder (°C)	Rpeak (% s^{-1})	Tpeak (°C)	RMx10³ (% s^{-1} °C^{-1})	Residue (%) (900°C)
CS	160 -452	0.028	197	0.041	260	0.21	13
RH	220 - 560	0.31	220	0.083	285	0.38	29
These values are in agreement with the results achieved by Munir et. al. [13].							

The RM (Reactivity Values) of CS is higher when compared with RH samples under oxy combustion atmosphere. Table 3 shows reactivity of CS and RH along with the reactivity values calculated by different authors. Combustion characteristics such as initial ignition temperatures, burn out temperatures, TGA and DTG curve are generally used to measure relative combustion characteristics of the biomasses [28]. As CS sample showed lower ignition temperature when compared with RH sample ignition temperature. This study is in agreement with the study performed on biomass and coal samples by [29]. Moreover, an ignition index (D) and combustion index (S) of the samples were calculated from the following equations [29].
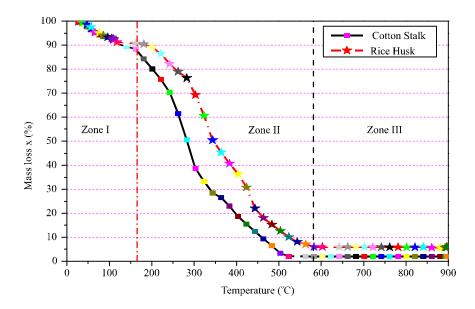

FIG. 4. TGA CURVE OF COTTON STALKS AND RICE HUSK SAMPLES UNDER OXIDATIVE ENVIRONMENT
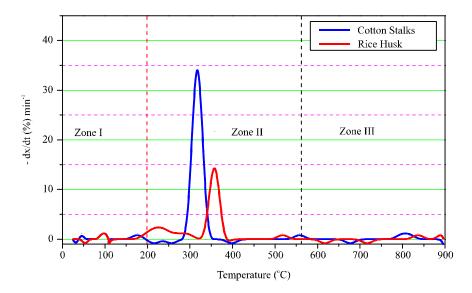

FIG. 5. DTG CURVE OF COTTON STALKS AND RICE HUSK SAMPLES UNDER OXIDATIVE ENVIRONMENT

$$D = \frac{R_{max}}{\left(t_{max} t_i\right)} \tag{2}$$

$$S = \frac{R_{max} R_a}{\left(T_i^2 T_b\right)} \tag{3}$$

Here, t_{max} shows a maximum rate of combustion t_i represents ignition temperature. R_{max} is the maximum reduction in mass. R_a represents the maximum reduction in mass under oxygen environment. The results of both samples are given in Table 4. It is obvious from the results that with the rise in ignition index (D) value, the ignition performance of biomass materials increases. Besides that, an enhanced burning reactivity may be given to the material showing the higher value of combustion index (S). The CS is more reactive material than RH. The apparent activation energy and order of reaction is shown in Table 5.

3.3   Kinetics of Waste Agricultural Biomass

The kinetic investigation has been done by using thermal analysis techniques in order to calculate the kinetic characteristics of biomass [30]. Numerous methods and approaches have been adopted to investigate the thermal behavior of different biomass materials using TGA. In this paper, investigation of kinetic parameters under inert and oxidative environments is calculated by using Arrhenius equation.

$$S = \frac{dx}{dt} kx^n \tag{4}$$

Where x shows conversion ratio and is represented as $x = \left(\frac{mo - m}{mo - mf}\right)$, m represents mass of sample at any time whereas 0 and f represent initial and final mass of samples at the end of the stage respectively. N and k are reaction order and reaction constants respectively. After combining the Equation (5), the combined Equations (4-5) becomes linear form Equation (6) represented as:

TABLE 3. KINETIC BEHAVIOR OF TGA EXPERIMENTS UNDER OXIDATIVE ENVIRONMENT

Biomass	DE Volatilization Zone			Char Combustion			Ash (%)	RMx10³
	Temperature Range (°C)	Rpeak (% s⁻¹)	Tpeak (°C)	Temperature Range (°C)	Rpeak (% s⁻¹)	Tpeak (°C)	(900°C)	(% s⁻¹ °C⁻¹)
RH	171- 360	0.064	365	370 - 580	0.316	375	7.4	0.63
CS	153 - 282	0.056	280	339 - 510	0.216	344	4.3	0.46
RM: Reactivity (% s-1oC-1)								

TABLE 4. COMBUSTION CHARACTERISTICS OF SAMPLES UNDER OXIDATIVE ENVIRONMENT

Sample	T_i	T_i (s)	R^a (10⁻² % s⁻¹)	Rmax (% s⁻¹)	Tmax (s)	Tb (°C)	Tb (s)	Dx10⁷	Sx10¹⁰
RH	230	2622	0.832	0.236	4631	413	2622	0.22	1.20
CS	223	2516	0.91	0.339	4516	408	2516	0.36	1.50

TABLE 5. APPARENT ACTIVATION ENERGY AND ORDER OF REACTION UNDER INERT AND OXY COMBUSTION ATMOSPHERES

Biomass	Pyrolysis			Oxy Combustion		
	E (kJmol⁻¹)	Regression (R²)	Order of Reaction (n)	E (kJmol⁻¹)	Regression (R²)	Order of Reaction (n)
RH	68.77	0.9877	0.76	118	0.998	0.94
CS	72.31	0.973	1.15	106	0.9988	1.04

$$k = A\exp\left(-\frac{E}{RT}\right) \quad (5)$$

$$\ln\left[\frac{-1}{mo-mf}\frac{dm}{dt}\right] = \ln(A) - \left(\frac{E}{RT}\right) + n\ln\left(\frac{m-mf}{mo-mf}\right) \quad (6)$$

Where dm/dt displays the ratio of change in mass with respect to change in time, R represents the universal gas constant, A is the pre-exponential factor. Where Equation (7) lead to linear form written as:

$$Y = B + CX + D*Z \quad (7)$$

Where

$$y = \ln\left[\frac{-1}{mo-mf}\frac{dm}{dt}\right], x = \frac{1}{T}, z = \ln\left(\frac{m-mf}{mo-mf}\right), B = \ln(A), C = -\frac{E}{R}, D = n$$

Here constants B, C and D are calculated by multi-linear regression of the TGA data for each stage using Microsoft Excel. The kinetic results were compared with the data available in the literature. RH samples have the higher values of activation energy 118 kJ/mole, ln A 19.2 s^{-1} while CS sample activation energy was 106 kJ/mole, ln A18.1 s^{-1} under oxy combustion atmosphere. Dorgeet. al. used the similar experimental and analytical method for Miscanthus. The order of reaction for both samples was observed from 0.76-1.15. A similar order of reaction was found by [16,21,31].

4.   CONCLUSION

The kinetic study of CS and RH revealed that in the first zone, reduction in mass was because of the moisture evaporation and volatile release observed in the temperature 22-155°C for cotton stalks and from 24-201°C for RH samples respectively. Whereas the devolatilIzation which is the main pyrolysis stage of mass loss was observed in temperature range from155-449°C for CS and for RH it was observed from 201-560°C, while the third stage of mass loss ranged from temperature from 449-900°C for CS and for RH samples was in temperature range of 560-900°C. The weight loss under oxidative environment in the first zone was observed from 23°C to nearly 145°C. At this stage of weight loss, evaporation of water and light molecules may have accounted for weight loss. The weight loss of CS and RH at second stage was observed

at temperatures between 153-580°C and at the third stage of weight loss that ranged from 580-900°C was due to the combustion of the sample under oxygen environment. It is estimated that maximum degradation rate occurred at 282 and 365°C for CS and RH samples respectively.The results reveal that the HHV of RH and CS possess good prospect for thermochemical conversion into value able biofuels. The HHV of RH and CS samples were found 15.36 and 16.81MJ/kg. The apparent activation energies under pyrolysis were 68.77 and 72.31 kJmol^{-1} under oxy combustion atmosphere 118 and 106 kJmol^{-1} for above sample sequence. The order of reaction (n) and regression coefficient (R^2) under both atmospheres for both samples were 0.76, 1.15, 0.9877 and 0.973 under pyrolysis whereas under oxidative atmosphere 0.94, 1.04, 0.998 and 0.9988 respectively. The results collected in this study reveal that the RM of CS samples were higher than RH samples under both nitrogen and oxygen atmospheres. The TGA and DTG curve presented lower degradation temperatures for CS samples than RH samples under both inert and oxidative environments.

ACKNOWLEDGEMENT

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