Thermo Gravimetric Study of Pakistani Cotton & Maize Stalk using Iso-Conversional Technique

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Abstract: Characterization is important to measure the potential of biomass for its utilization in combustion or pyrolysis processes. Characterization study is carried out for cotton and maize stalk samples collected from the provinces of Punjab and Sindh, Pakistan. The proximate, ultimate and thermo-gravimetric analysis (TGA) are performed. TGA is done in inert atmosphere at four heating rates i.e. 5, 10, 15, 20°C/ min. Residual weight is a function of heating rate and increases with heating rate. Higher residual weight is obtained for cotton stalk at different heating rates from 5 to 20°C/min. The values of energy of activation for cotton and maize stalk are 35 and 40 kJ/mol respectively which is calculated using isothermal conversion method assuming first order kinetics.
[Ali N, Saleem M, Kamil M, Shahzad K, Chughtai A. **Thermo Gravimetric Study of Pakistani Cotton & Maize Stalk using the Iso-Conversional Technique.** *Life Sci J* 2014;11(8):382-387]. (ISSN:1097-8135). http://www.lifesciencesite.com. 50

Keywords: Thermo Gravimetric, Biomass, Activation Energy, Fast Pyrolysis

1. Introduction

Biomass is a renewable energy source, [1]. Biomass energy can be utilized after necessary conversion like combustion, gasification, pyrolysis etc. Selection of energy conversion technique is dependent on the characteristics of biomass. Pakistan is an agricultural country and produces crop residues of about 84 million tons per year, out of which 69 million tons are field based crop residues [2]. Effective utilization may be achieved via adopting modern energy conversion techniques like gasification and pyrolysis. [3]. Cotton and Maize Stalks are the field based agricultural residues which are byproduct of cotton and maize crops. Pakistan comes on the 4th position among the largest cotton producing countries in the world which produces 9.7 million bales per year contributing 8.81 % of total world [4]. The annual production of cotton stalks is around 13.20 million tons. Maize enjoys an important position in the existing cropping systems of Pakistan. It ranks third after wheat and rice in Pakistan for its grain production.

Cotton and Maize stalks are the source of green energy with considerable high heating values (15-18 MJ/Kg) [5, 6], therefore thermochemical processes such as pyrolysis and gasification can be used to convert these residues into useful energy [7]. Pyrolysis produces 60-75 % bio oil, 15-25% solid char and 10-20% non-condensable gases subject to the biomass materials [8, 9]. Characterization studies of the Cotton and Maize stalks have already being reported [3, 4, 10]. However, since physical and chemical properties of biomass depend on the origin which affect its behavior in thermo-chemical conversion processes.

In this study, thermo gravimetric analysis of Pakistani cotton and maize stalks is done to calculate the activation energies using the Iso-conversional plot. The biomasses were collected from two provinces of Pakistan.

Moisture contents of biomass varies in the range of 3 % to 63 % and vary in the case of force drying [3]. The volatile matter present in a biomass varies from 48% to 86 % on dry basis due to location and maturity level of the plant at the time of cultivation [4]. Ash content may be in the range of 0.1 to 46 % on the dry basis [4]. Ash causes problems like sintering, agglomeration, deposition, erosion and corrosion due to its low melting [11]. The alkali silicates and sulfates present in ash have melting points even lower than 700°C which tend to deposit on the reactor walls and leave a sticky deposit on the surface of the bed particles [11].

Ligno-cellulosic biomass has heating values in the range of 15-19 MJ/kg [4]. Cellulose fibers provide strength to the structure of the plant which is around 40 to 50 % in wood [12]. The structure of cellulose is a liner polymer type and its reported molecular weight is more than 10^6 kg/kmole. Cellulose degradation occurs between the temperature ranges of 240 to 350°C [10]. Hemicellulose (Polyose) is also a major chemical constituent of biomasses. It is a mixture of various polymeric components such as glucose, mannose, galactose, xylose etc. The molecular weight of hemicellulose is lower than that of the cellulose [10,

12]. The decomposition of hemicellulose starts between 200 to 260°C. Lignin varies between 16 to 33 % with no fix structure and is a cross link resin. Lignin gives rigidity to the plant. Its degradation temperature ranges from 280 to 500°C [13].

In thermo gravimetric analysis, sample can be subject to the gradual heating under conditions similar to combustor, gasifier, or pyrolysis process. The weight loss versus temperature data provides insight of the thermo chemical conversion behavior of the fuel. When performed in inert environment, the process can be split into four zones as: (I) moisture evolution zone, (II) active pyrolysis zone (major degradation zone in which most of the de-polymerization occurs), (III) passive pyrolysis zone and (IV) slow degradation zone. Over 120-170°C, a small amount of weight loss results due to light weight volatile compounds . This zone is defined as preheating period where mainly moisture is considered to be evaporated. Active pyrolysis zone ranges over 170-320°C. The maximum amount of biomass is decomposed in this stage. Thereby, a major weight loss is perceived in this zone. The passive pyrolysis zone prevails over 320-580°C. There the TGA curves show a minor change in slope which guesses the second reaction zone. The two zones (active and passive) are the main pyrolysis zones because thermal decomposition of hemicelluloses and cellulose takes place in the active zone while the conversion of lignin occurs in the passive zone. Finally over 580-750°C, carbonization zone is identified in which char and ash is formed. Further loss in weight of samples is minimal during and after this zone. Iso-conversional technique can be employed for the estimation of energy of activation from the thermo gravimetric data assuming 1st order kinetics.

2. Materials and Methods

Cotton and Maize stalk samples were collected from the village of Sahiwal, District of the Punjab and from the province of Sindh. The sun dried samples are reduced down to the particle size of 1-3 mm using rotary cutter and grinding mill. The final samples are stored in air tight plastic containers for further use. The proximate analyses are performed using a Leco TGA-701 analyzer. The ultimate analysis is carried out with a Vario Micro CHNS Analyser. Higher Heating Value (HHV) is determined with the help of auto bomb calorimeter.

TGA analyses are performed using SDT Q600 simultaneous TGA/DSC thermal analyzer with heating rates ranging from 5 to 20 °C/min under constant flow condition of nitrogen (100 ml/min). The initial and final temperatures are 30°C to 800°C respectively. The initial degradation temperature, rate of thermal degradation and residual weight at a temperature of 700°C are derived from weight loss and temperature data. The chemical composition (cellulose, hemicellulose and lignin) of cotton and maize stalk is determined according to standard analytical methods used in the pulp industry.

Table 1: Proximate Analysis of Cotton & Maize Stalk.

Parameters	Cotton Stalk	Maize Stalk
Moisture	00.49	01.10
Volatile Matter	63.21	63.27
Fixed Carbon	31.03	30.02
Ash	03.76	04.19
Elemental Composition (%)		
Carbon	41.84	43
Hydrogen	5.96	5.8
Nitrogen	0.51	0.94
Sulphur	0.11	0.12
Oxygen	51.58	50.14
HHV (MJ/Kg)	16.67	15.99
Chemical Composition (%)		
Cellulose	27.50	29.70
Hemicellulose	25.40	16.80
Lignin	21.70	17.00

3. Results and Discussion

3.1 Thermo gravimetric Analysis

The proximate and ultimate analysis of the samples is given in Table 1. The moisture content determined in the cotton and maize stalks is 0.49 % and 1.1 % respectively which is quite less perhaps due to the sun drying of the sample.

Volatile matter, 63.21% and 63.27% respectively for cotton and maize stalks is slightly lower than the reported values in the literature [4]. Volatile matter may also vary due to location and maturity level of plant at the time of cultivation [14, 15]. Ash content of cotton and maize stalk is 3.76% and 4.19% respectively, which is within the reported range. Biomass with higher percentage of ash contents is more suitable for gasification and pyrolysis, than combustion due to lower operating temperatures.

The values of carbon content are 41.84 and 43% in the studied cotton and maize stalks respectively which can be linked to the relatively lower heating values of cotton and maize stalks. The values of hydrogen content measured for cotton and maize stalks are 5.96 % and 5.8 % respectively which are almost similar to those values reported in literature [2]. The percentage values of nitrogen in cotton and maize stalks are 0.51 % and 0.94 % respectively.

Sulphur contents of cotton and maize stalks are 0.11 % and 0.12 % respectively. The percentage of oxygen is high in both biomass samples under

investigation. Oxygen to hydrogen ratio can be taken as a deciding factor for the selection of thermo chemical conversion process for a particular fuel. The gross calorific values of cotton and maize stalks are 16.67 and 15.99 MJ/kg respectively which are well within the range of reported values.

Cellulose fibers provides strength to the structure of plant and normally higher in wood around 40 to 50 % [12]. The structure of cellulose is a liner polymer type and its reported molecular weight is more than 10^6 kg/kmole. Cellulose degradation occurs between the temperature ranges of 240 to 350°C [10]. The values of cellulose for investigated samples of cotton and maize stalks are 27.5 % and 29.7 % respectively which is lower than the average literature values. Hemicellulose (HC) in the tested sample is 25.40 % and 16.8% for cotton and Maize stalk respectively. The HC is within the reported range for cotton stalk while lower for the Maize stalk. Lignin varies between 16 to 33 % in the wood normally. Its degradation temperature ranges from 280 to 500°C. The amount of lignin reported in cotton and maize stalks is 21.7 % and 17.0 % respectively. Maize stalk contains lesser percentage of the sum of cellulose and hemicelluloses (46.5%) than that of cotton stalks (52.9 %) which explains the low HHV of the maize stalk.

3.2 Thermo gravimetric Analysis

The results of TGA analysis of cotton and maize stalks at four heating rates (5, 10, 15, 20°C/min) are shown in Figure 1 to 6 . The weight percent versus time data are depicted in Figure 1 and Figure 2 for cotton and Maize stalks respectively. The curves are nearly horizontal at the beginning eventually descending steeply and shifting towards the constant values Total time of analysis decreases for high heating rates. The steepness reflects the fastness of volatilization of the samples resulting in loss of sample weight. The final weight is the residue or ash.

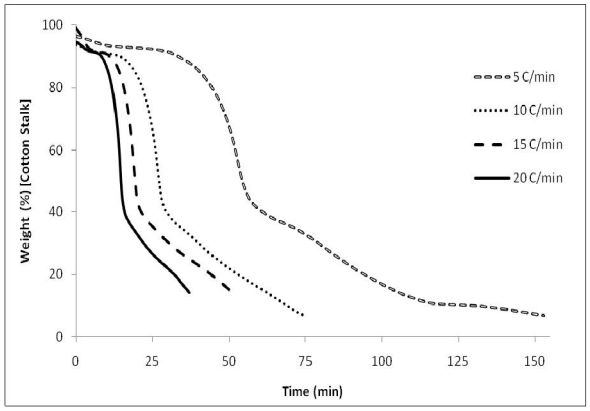

Figure 1: weight Percent vs time curves of Cotton stalk sample at different heating rates.

Since the devolatilization is strongly dependent on temperature, so presenting the weight loss versus temperature will be more useful for analysis as shown in Figure 3 and Figure 4. In all cases moisture is removed up to 100°C.

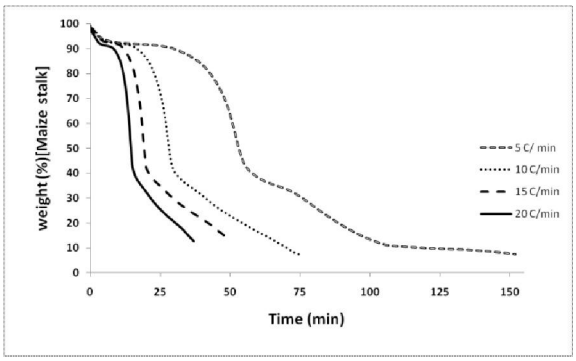

Figure 2: weight Percent vs time curves of Maize stalk sample at different heating rates.

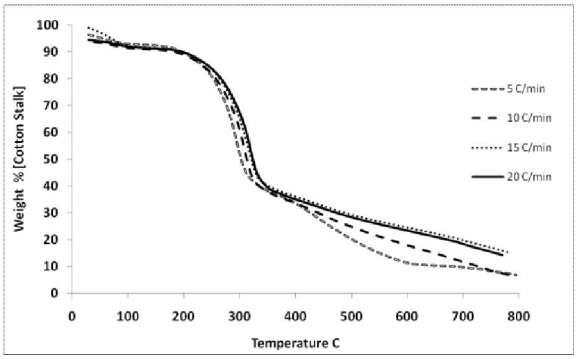

Figure 3: Percent weight vs temperature curves for Cotton stalk samples at various heating rates.

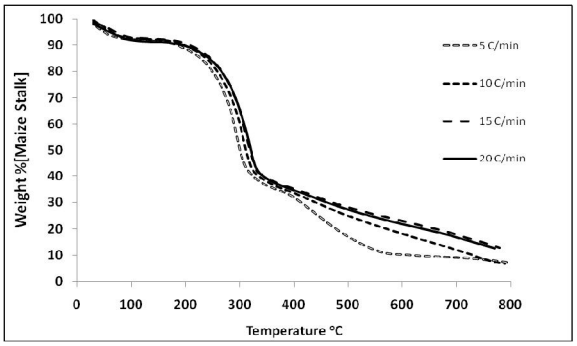

Figure 4: weight Percent vs temperature curves for Maize stalk samples at various heating rates.

After 200°C weight loss starts quickly and continue to decrease up to 350°C. After 350°C weight loss continues but at lower rate In the maximum weight loss zone, the curves slightly shift to the right at the higher heating rates. The behavior of both the biomasses is almost similar.

The weight of solid residue after the pyrolysis increases with the heating rate for both samples as shown in table 2. Residual weight at a specific heating rate is higher for cotton stalk except 10 ^{o}C/min. More conversion of maize stalk implies its more suitability for pyrolysis as compared to the cotton stalk. During the thermal conversion process of maize stalk samples, more biomass is converted into gaseous products as compared to the cotton stalk.

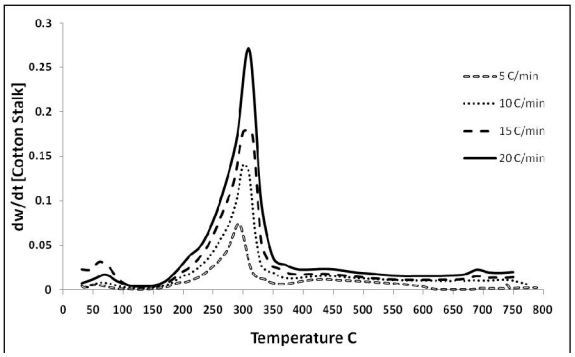

Figure 5: DTG curves for Cotton stalk samples at different heating rates

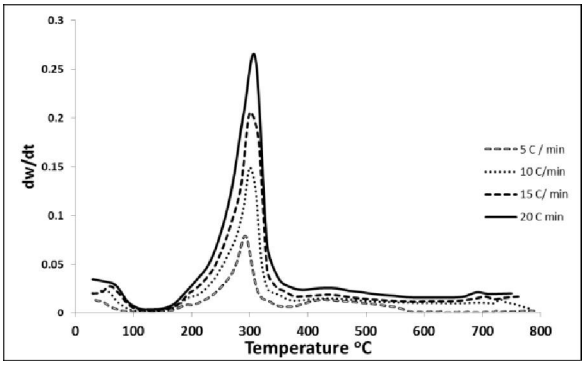

Figure 6: DTG curves for Maize stalk samples at different heating rates

Data for the differential weight percent loss versus temperature is depicted in Figure 5 and Figure 6. The change of the rate of devolatilization versus temperature is very clear. The devolatilization rate is maximum around 300^{o}C and maximum weight loss occurs over 200-350^{o}C. Obviously the peaks are higher at higher heating rates. The time rate of percent weight loss tends to approach zero in all cases.

Table 2: Thermal degradation characteristics of Cotton and Maize stalk samples derived from TGA

Heating Rate (^{o}C/min)	Thermal Degradation at Temperature Zones(%)				Initial Degradation Temperature (^{o}C)	Residual Weight at 700^{o}C (%)
	120-170 ^{o}C	170-320 ^{o}C	320-580 ^{o}C	580-750 ^{o}C		
Cotton Stalk						
5	0.91	49.19	30.06	4.32	170	9.71
10	0.73	45.76	25.37	10.71	180	11.80
15	0.51	40.04	25.81	8.35	195	19.67
20	0.50	37.44	29.07	8.86	210	18.34
Maize stalk						
5	1	49.99	30.16	2.31	170	7.373
10	0.76	47.49	24.49	10.781	185	6.938
15	0.89	49.16	18.82	8.91	200	12.82
20	0.51	47.71	20.93	8.52	210	12.52

Table 3: Energy of Activation for Cotton Stalk

X	R^2	Equation	m	Ea	C	A
--	--	--	--	kJ/mol	--	1/min
0.3	0.92	y = -2187.6x + 8.2886	-2187	17.3	8.3	276.8
0.4	0.99	y = -2021.5x + 8.0463	-2021	15.9	8.0	201.5
0.45	0.99	y = -2032.1x + 8.0437	-2032	16.1	8.0	183.2
0.5	0.99	y = -2087.5x + 8.0935	-2087	16.5	8.1	170.5
0.55	0.99	y = -2349.3x + 8.3804	-2349	18.6	8.4	181.6
0.6	0.93	y = -4480.3x + 10.803	-4480	35.4	10.8	954.3

Table 4: Energy of Activation for Maize Stalk

X	R 2	Equation	m	Ea	C	A
--	--	--	--	kJ/mol	--	1/min
0.3	0.87	y = -3770.2x + 10.202	-3770.2	29.8	8.3	160.6
0.4	0.79	y = -4432.7x + 10.901	-4432.7	35.0	8.0	91.9
0.45	0.97	y = -4462.2x + 10.899	-4462.2	35.3	8.0	83.4
0.5	0.99	y = -4131.4x + 10.48	-4131.4	32.6	8.1	86.1
0.55	0.99	y = -4406.8x + 10.768	-4406.8	34.8	8.4	96.8
0.6	0.98	y = -5094.3x + 11.524	-5094.3	40.3	10.8	839.3

The maximum decomposition rate is observed at 20°C/min at a temperature of 330°C for cotton stalk. Pyrolysis rate also increases with the increase of heating rates under the same condition of inert gas in case of both biomasses under investigation.

Figures 3 and 4 reveal that the total weight loss during pyrolysis is rapid at higher heating rate for both types of biomasses. Almost 80% and 85% weight is lost in 30 and 85 min at the heating rates of 20 and 5 °C/min respectively for the maize stalk sample (Figure 2). The same trend is observed for cotton stalk sample.

The maximum degradation rate at various heating rates is lower in case of cotton stalk upto 15°C/min in contrast to the results at 20°C/min. The maximum degradation occurs at heating rate of 5°C/min for cotton and maize stalks which is 4.4 %/min and 4.7 %/min respectively. The maximum and minimum percentage of weight loss is observed at the same temperature for cotton and maize stalks.

3.3 Energy of Activation

Energy of activation is being discussed by many researchers [16-18]. The energy of activation gives an idea that how much energy will be required during the pyrolysis process for producing the different products. Energy of activation for cotton and maize stalks are calculated from the Figure 7 and Figure 8 and tabulated in table 3 and 4 respectively. Calculations was done using the MATLAB software.

It is concluded from the experimental data that energy of activation changes with the extent of reaction for both samples of biomasses under study. The effect on energy of activation with the conversion is less dependent for maize stalk than that of cotton stalk. It means that initial degradation for cotton stalk is easy. Relatively high energy will be required during the pyrolysis for maize stalk. Energy of activation reported in literature for cotton and maize stalks are 77 and 50 kJ/mol respectively, which are higher as compared to the measured values of 35 and 40 kJ/mol for Pakistani cotton and maize stalks respectively. The reason may be the higher amount of oxygen present in the samples which promote the chemical reaction during thermal conversion process (pyrolysis) and lowers the energy of activation.

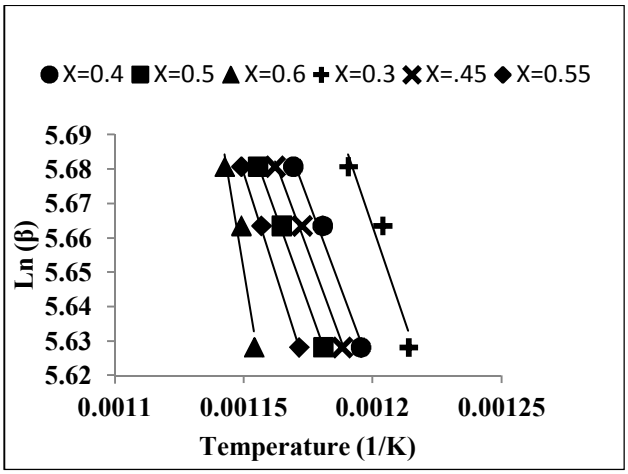

Figure 7: Iso-conversional plot for Cotton Stalk

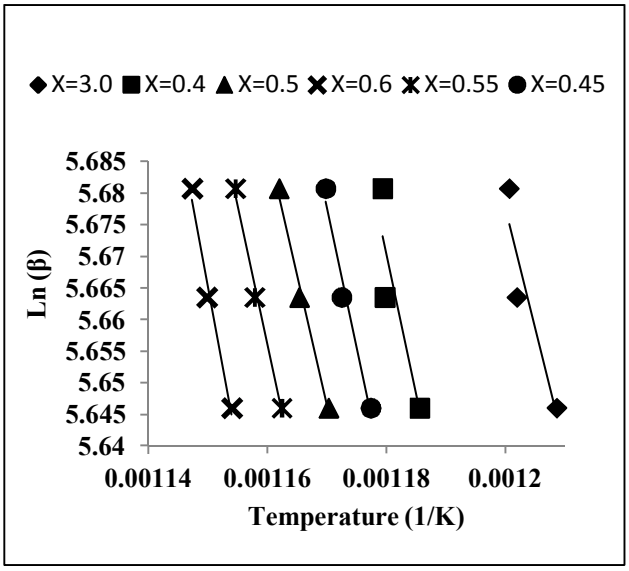

Figure 8: Iso-conversional plot for Maize Stalk

4. Conclusions

Maize stalk gives higher percentage of liquid and gaseous products as compared to cotton stalk at different heating rates. Residual weight of maize stalk is relatively lower as compared to cotton stalks which may cause removal issues in the case of cotton stalks. For controlling the residual solid problem in

case of cotton stalk, gasification process is a better option. Since oxygen to carbon ratio of cotton stalk is more than 1 (1.23), hence there is no need of additional oxygen during gasification for producing syngas which is also an additional advantage.

Acknowledgement

The authors acknowledge the financial support of University of the Punjab and Higher Education Commission, Pakistan and the cooperation extended by the department of Polymer Technology, University of the Punjab and GC University, Lahore as well as Prof. Dr. Shahid Munir for useful discussions.

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