

Micro and Macro Thermal Degradation Behavior of Cotton Waste

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Abstract

Fulfillment of energy demand and simultaneously to find proper solution of MSW from economical, social and environmental point of view waste-to-energy is the best option; also, the energy crisis is the new challenge in the front of world to push the economy in the progressive direction and simultaneous global warming and efficient use of energy are also challenging tasks. The thermal degradation of cotton was studied at temperature values (β) of 5,7,10,15,20 °C/min in a nitrogen atmosphere utilizing the TG/DTG 32 horizontally differential systemic balance method, which occurs in three stages. The three separate independent parallel mechanism's defining the degradation was considered to derive the kinetic parameters. In first and second stage there might be degradation is with 10-15 % of total weight and 60-70 % of total weight respectively and finally 4-9 % residue remains in case of all heating rate. The elemental analysis of residue shows the existence of different elements in the residue on basis of which possible pollutants and cleaning requirement of thermal conversion system can be decided. The current TGA data was compared to sample decomposition using a Batch Type Pyrolyser (BTP) with a sample weight of 60 gm and a heating rate of 10 °C/min in a nitrogen atmosphere. The information obtained will aid in the modelling, designing, and operations of MSW thermal conversion methods.

Key-words: Cotton Waste (Textile Waste), Kinetics, Elemental Analysis and Batch Type Pyrolyser.

1. Introduction

Human emissions generate trash, and how these pollutants are managed, kept, gathered, and dispose of which can pose serious environmental and health risks. Wherever there is a concentration of human activity, such as in cities, efficient and safe solid waste management is critical in order to provide healthy environment for the inhabitants. Energy usage, Waste output, and Greenhouse gases

will rise as fast as economy and population expansion continues. These are significant challenges for the international community. In India waste generation is 196 MT per year ^[1] and due to lack of recourses and due to lack of good governance the solid waste management is serious issue; to overcome energy crisis problem waste-to-energy is more appropriate solution. The lack availability of land for land filling and due to environment problem related to incineration is not acceptable option and so pyrolysis is good option.

The India is 4th largest country of the world in cotton production and average 2.5 to 3.5 % textile waste majority cotton waste is in MSW composition of India ^[1, 2]. The understanding of degradation behavior of cotton waste is having very good strength to understand pyrolysis of cotton waste and possible estimation of yield products. The kinetics study of cotton waste play an important role to know its degradation behavior and stages of degradation as well as estimates kinetics parameters such as activation energy (E) and frequency factor (logA) which conclude how fast cotton waste composition get degraded and liberated the energy in the form of yield products for various temperature levels. The kinetics parameters can be determined by using analytical methodology called Thermo Gravimetric Analysis (TGA).

The cotton is cellulosic composition and so degradation behavior is similar to other cellulosic waste. Várhegyi created an effective approach that assumes parallel, independent reactions in the case of biomass products arising from a single source. A linear combination of such reactions determines the overall rate of the reaction. A conversion (reacted fraction) and a reaction rate are established for each reaction (reactant) to their own kinetic formula and variables ^[3, 4, 5]. R. Miranda ^[6] reported on the thermal characteristics of textile waste, which was investigated using thermogravimetry at various heating rates as well as semi-batch pyrolysis. Three peaks can be seen on the DTG curvature, two of which are hemicellulose & cellulose, and one of which could be a synthetic polymer. The pyrolysis substances were collected using bench scale pyrolysis testing. Julia Molto ^[7] have studied weight loss behaviour of cotton waste in inert gas as well as in air atmosphere for three heating rates 5, 10, 20 °C/min.

The kinetic models for MSW pyrolysis were determined by A.N. Garcia et al ^[8]. Wu et al. ^[9] investigated the kinetics of pyrolysis of a combination of 4 papers (unlaminated and laminated printing paper, newspaper, and tissue paper) at temperature levels of 1, 2, and 5 K/min, finding that degradation took place in two phases. At a heating rate of 10 °C/min, L. Sørum et al ^[5] recorded degradation with four kinds of papers and five different plastics. With the exception of poly vinyl chloride, the results show that paper degradation occurs in three phases and plastic decomposition occurs in one stage when using a single reaction concept with parallel and independent reactions. JIN

Yu-qi et al ^[10] investigated a new reaction kinetics in which the number of losing weight phases is equivalent to the number of reactions. Wu et al ^[11] examined the decomposition of newspaper using a TGA machine at a constant heating rate of 5 K min⁻¹ in a nitrogen environment, analyzing the pyrolysis byproducts and collecting the residues using a GC and an elemental analyzer, respectively. TGA tests for newspaper at heating rates of 5, 10, and 20 K/min were published by Bhuiyan et al ^[12] for kinetic investigations as well as pyrolysis on newspaper waste.

P. Grammelis et al ^[13] used thermogravimetry to investigate the behaviour of refuse-derived fuels during pyrolysis and combustion. With the base of a sequence of TGA studies for cardboard, C. David et al ^[14] addressed the pyrolysis process. The goal of Kuen-Song Lin ^[15] was to get RDF of pyrolysis and kinetics in order to better understand the function of its elements in pyrolysis behavior. The thermo gravimetric analyzer was used to evaluate the early pyrolysis kinetics of RDF. Ch. Pasel ^[16] discusses the technical prerequisites for an engineering application of pyrolysis of shredder trash as a feasible method for chemically recycling of plastic waste. Pyrolysis, according to S. Ojolo ^[17], is a potential method for turning MSW into fuels and managing wastes through reduction in volume. Samit Kumar Singh et. al ^[18] focused on effect of heating rate in case of various paper waste residues of MSW to estimate variation in elemental percentage at various heating rates. Samit Kumar Singh et. al estimated kinetic parameters of cotton polythene mixture and cardboard waste too ^[19, 20].

Even though waste-to-energy is a great alternative, several info regarding pyrolysis and kinetics is mandated for constructing incinerators, gasifiers and pyrolyzers for biomass waste but info is insufficient for newspaper trash. A kinetic research has been conducted at the micro scale, however a kinetic study at the macro scale is still not disclosed to our information.

The goal of this research is to calculate the kinetic parameters of cotton waste at various heating rates 5,7,10,15,20 °C/min (β) and determination of elements exist in residue of cotton waste for heating rate 10 °C/min and 20°C/min. The elemental analysis of residue remain after were carried out in Scanning Electron Microscope (SEM - JEOL 5610LV) with Energy Dispersive Spectroscopy (EDS).

2. Experimental

2.1 Materials

Cotton was collected from a nearby store and cut into strips of 2-3 mm with stainless steel scissor for the experiment. Due to the lack of size and weight constraints in the crucible, the size of

the particles employed in BTP is bigger than in TGA. The proximate and ultimate analysis data as well as the HHV of cotton waste are shown in Table 1.

Table 1 - Proximate Analysis, Ultimate Analysis and Higher Heating Value

Fixed Carbon (% wt)	Moisture (% wt)	Volatile Matter (% wt)	Ash (% wt)	Carbon (% wt)	Hydrogen (% wt)	Nitrogen (% wt)	Sulfur (% wt)	Oxygen (% wt)	HHV MJ/kg
5.7	3.61	89.3	1.39	45.92	6.05	0.12	0.57	0.00	17.87

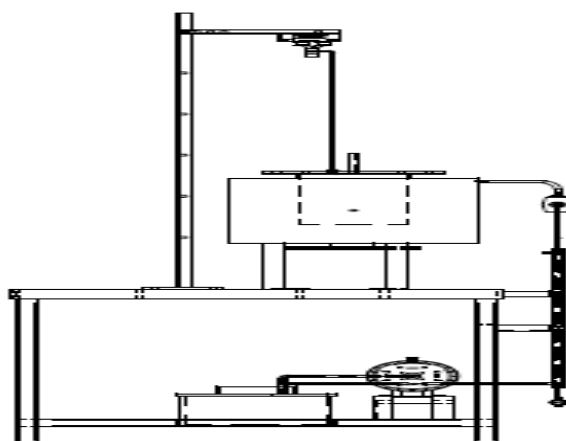
2.2 Thermogravimetric Analysis (TGA)

The SEIKO TG/DTA-32 thermal system is used for thermo - gravimetric & differential thermogravimetric measurements. Samples was examined from room temp to 600 °C at a temperature level of (β) 5, 7,10,15,20 °C/min in a nitrogen gas environment at atmospheric pressure and a flow rate of 50 ml/min. The maximum size of sample utilized is 6 mg. The samples were placed in a platinum crucible with alfa alumina serving as a standard.

2.3 Batch Type Pyrolyser

Pyrolysis of newspapers were performed in a Batch Type Pyrolyser (BTP) using a PLC control system to achieve various heating rates in the range of temperatures of RT to 1200 °C as shown in figure 1. The volatiles generated inside the reactor were condensed using a concentric tube heat exchanger. With a sample size of roughly 60 gm, the nitrogen purge rate being 2 lit/min and the heat rate was 10 °C/min at RT to 600 °C. Two thermocouples have been installed to monitor the temperature of both the heater and the sample.

Figure 1 - Batch Type Pyrolyser



3. Kinetics

Considering the TG/DTG curves may essentially been characterized by a fairly basic model of independent parallel processes is a fairly straightforward approach for calculating the kinetics of thermal degradation. This simplistic model believed that the sample's thermal characteristics may be expressed as the summation of its constituent components' behaviors [3, 4, 5, 6].

3.1 Kinetic Modeling

Due to the existence of several complex parts and their simultaneous and successive reactions, non-isothermal kinetic investigation of losing weight during pyrolysis of carbonaceous substance is a very difficult task. The term x defines the extent of transformation or just the percent of pyrolyzed substance.

$$x = \frac{m_0 - m}{m_0 - m_f} \quad (1)$$

Where m is the sample mass at time t ; m_0 and m_f are the readings at the begin and end of mass event of interest respectively.

$$\frac{dx}{dt} = k(T)f(x) \quad (2)$$

Where $f(x)$ is a dependent kinetic model function and $k(T)$ is a temperature-dependent reaction rate constant. There is also an Arrhenius type interdependence between $k(T)$ and temperature wrt Eq. (3).

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

Where A is pre-exponential factor (which is normally believed to be temperature independent), E is apparent activation energy, T is absolute temperature and R is gas constant. Whenever the temperature changes over time with such a constant temperature $\beta = \frac{dT}{dt}$, it is said to be non-isothermal. Eq. (2) is changed in the following way:

$$\beta = \frac{dT}{dt} = A \exp\left(\frac{-E}{RT}\right) f(x) \quad (4)$$

The usage of Eq. (4) assumes that the time evolution of a physical or chemical change is described by a kinetic triplet (E , A , $f(x)$). After integration, Eq. (4) yields:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = \frac{AE}{\beta R} p\left(\frac{E}{RT}\right) \quad (5)$$

Where T_0 = starting temperature, $g(x)$ = integral form of their action model and $p(E/RT)$ = temperature integration, which has no analytical expression. When T_0 is low, it is reasonable to suppose that $T_0 \rightarrow 0$, and therefore T_0 could be approximated to zero as the lower limit of integral upon on right-hand side of Eq. (5).

Doyle's approach ^[23] is used in the iso-conversional integral approach proposed independently by Flynn and Wall ^[21] and Ozawa ^[22]. This method is based on the following equation.

$$\ln \beta = \ln [AE/Rg(x)] - 5.331 - 1.052 E/RT \quad (6)$$

For $x=\text{const.}$, the plot $\ln \beta$ versus $(1/T)$, generated from thermo grammes measured at various heating rates has to be a straight line which slope could be used to calculate the actual activation energy.

In the instance of BTP, the Coats-Redfern technique ^[24] was employed to estimate kinetics presuming the reaction is first order.

The losing weight or conversion is changed to a normalized form α and this is referred to as response progress with temperature. The reaction progress under non isothermal TGA is described by

$$\alpha = (m_0 - m_T) / (m_0 - m_\infty) \quad (7)$$

When m_T = weight of sample at temperature T , m_0 = start weight and m_∞ = ultimate sample weight.

The Arrhenius parameters for said thermal breakdown of the materials were calculated by considering ^[22]. The integral formulation of rate law is used in this procedure. Any solid phase

reaction's rate law can be written as $d\alpha/dt = Ae^{-E/RT}(1-\alpha)$ (8)

The heating rate is considered as a function of time in non-isothermal TGA tests.

$$d\alpha/dt = d\alpha/dt * dt/dT \quad (9)$$

$$dx/dt = d\alpha/dt * 1/\beta \quad (10)$$

When β = heating rate given by dT/dt

$$d\alpha/dT = (A/\beta) * e^{-E/RT}(1-\alpha) \quad (11)$$

Assuming a first-order reaction, by integrating and calculating logarithms on both sides, we obtain

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT} \quad (12) \quad \text{for } n=1$$

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (13) \quad \left(\text{since } \frac{2RT}{E} \ll 1 \right)$$

The activation energy and frequency factor can be determined by plotting $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$.

4. Results and Discussion

4.1 TGA-based kinetics

Figure 2 - TG Curves; Figure 3 - DTG Curves

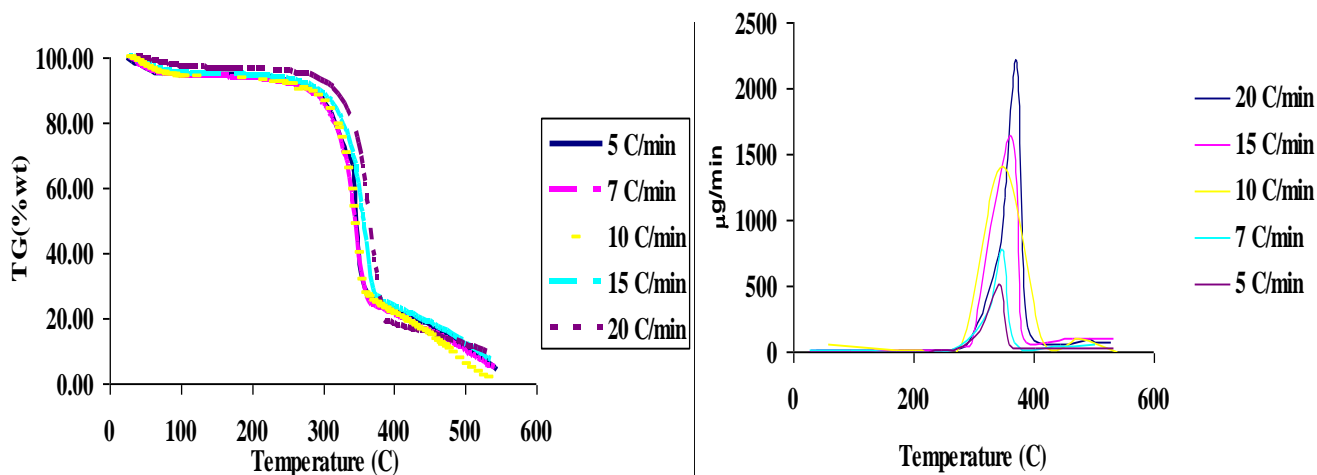


Figure 2 shows the degradation of cotton with respect to temperature occurs in three phases. In first phase hemicellulose may get decomposed and also moisture existing in the specimen may be removed and the degradation is slow due to high thermal resistance of system irrespective of heating rates in second and third phase, cellulose and synthetic materials are degraded, respectively. Figure 2 also shows that in case all five heating rates the TG curve patterns are same only the degradation rates different. The second stage degrades at a quicker rate than the first and third phases, and when the heating rate increases, the deterioration rate accelerates. In comparison to the previous heating rate, weight loss rises at a quicker pace in all three stages. The temperature range for all three phases varies from 30-280 °C, 280- 450 °C and 450-535 °C respectively. In first and second stage there might be weight loss of 7-10 % of total weight 60-70 % of total weight respectively and finally in third stage decomposition is 15-18 % & also 4-9 % residue remains respectively.

DTG curves are shown in Figure 3. Due to a combination of heat transfer at various heating rates as well as the kinetics of degradation leading in delay degradation, there seems to be a laterally movement towards elevated temperature of DTG curves and the readings of DTG rises as heating rates rises.

Figure 4 - Activation Energy and Frequency Factor for Textile Waste Composition

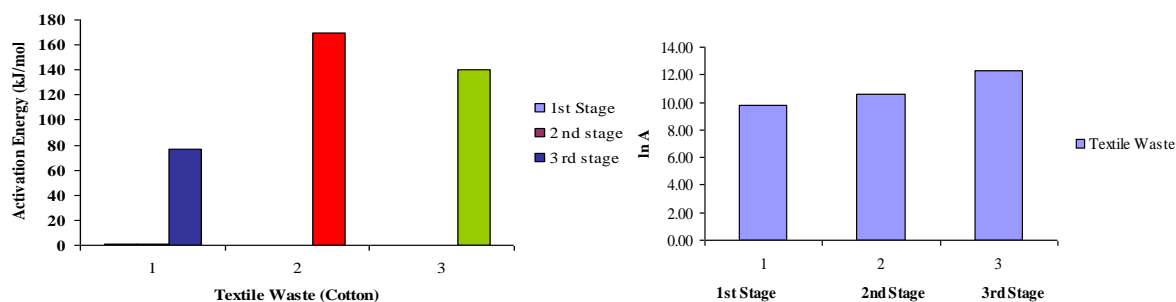


Figure 5 - T_{\max} Corresponding to DTG_{\max} for Textile Waste Composition

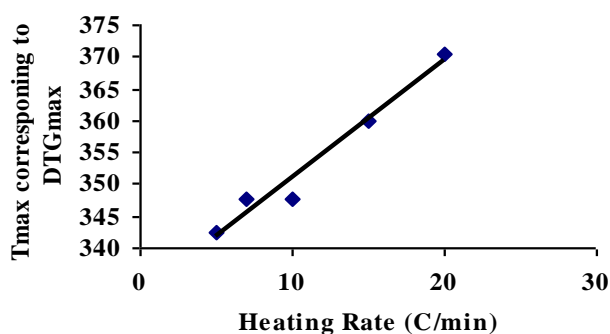


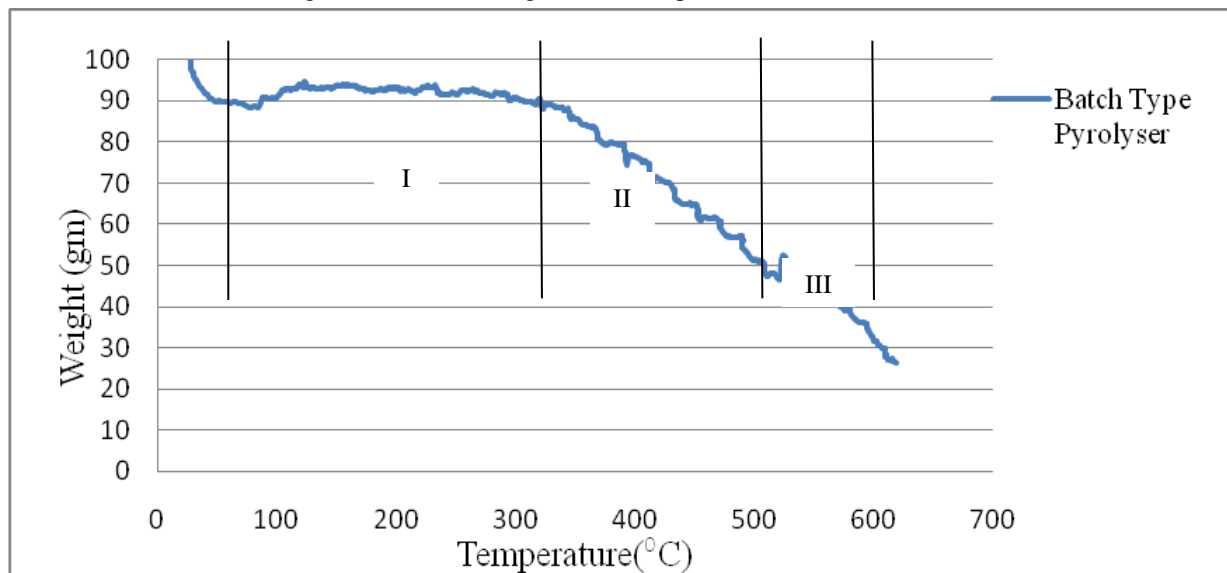
Figure 4 shows the readings of kinetic constants at various heating rates and the values increase with increase in heating rate. This also shows that while in the case of three phases, the kinetic constant is at its highest in the second phase. Figure 5 shows maximum decomposition corresponding to maximum decomposition rate of textile waste. Figure 5 depicts the maximum DTG temp and the accompanying heating rates which indicates that as heating rates increases, the degradation occurs at a faster rate and maximum degradation temperature also increases and due to which high amount of residue remains. Figure 4 also indicates that in second and third stage the activation energy increases due to high heating rates. The results show similar trend and values as other researcher [6].

4.2 Kinetics Model of a Batch Type Pyrolyser

The waste from textile is also cellulosic material and therefore the degradation of textile waste is similar to other paper wastes. The textile material is formed and it is decomposed at faster rate in second stage compare to any other cellulosic waste [5, 6]. In first stage the weight loss may be low due to presence of moisture content in the sample. Figure 6 shows that in second phase and third phase where degradation occurs at quicker pace, the value of activation energy is higher compare to first

stage where with decomposition the moisture which was trapped in the composition also released and with increase in temperature. Similarly, as the temperature rises, the value of $\log A$ rises due to enchantment in molecular collisions. Figure 6 additionally demonstrates that the values of activation energy are same in second phase and third phase of decomposition and values are quit higher compare to first stage. Some deviation is seen in the decomposition curve due to gases evolved through the crucible due to which some small jerks are created.

Figure 6 - Loss of Weight w.r.t. Temperature for Textile Waste



4.3 Comparative Study of TGA and BTP

Figure 7 - Comparative Study of TGA and BTP

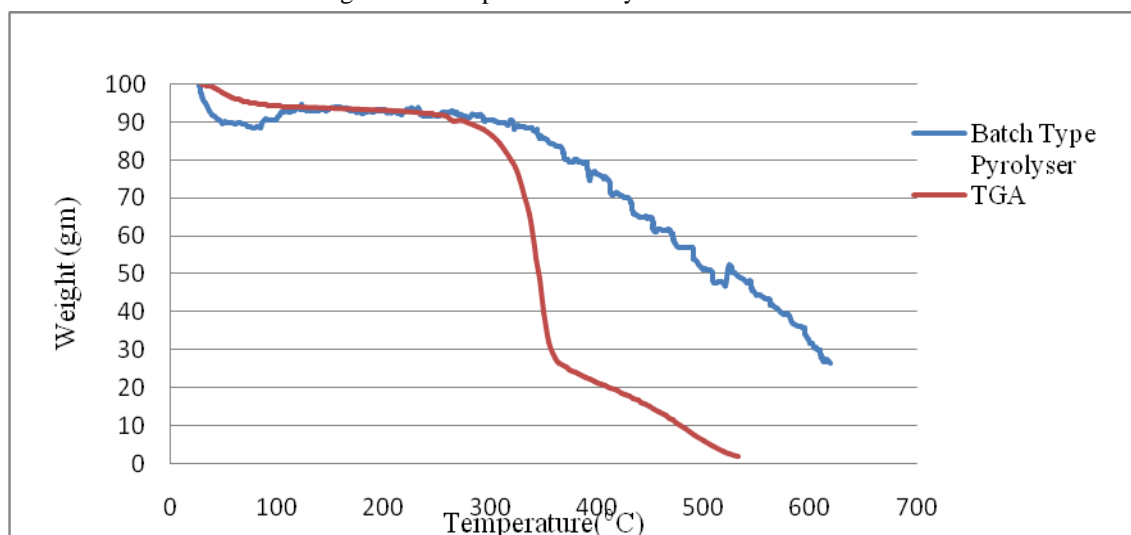


Figure 7 shows three stages of decomposition with corresponding temperature values which shows the decomposition trend is similar to paper wastes and decomposition occurs in the same range of temperature. The decomposition in first stage is almost same but in second phase and third phase, the weight loss is lower in case of BTP compared to TGA due to size of reactor, quantity of sample and flow of nitrogen etc.

Table 2 - Decomposition Stage Corresponding to Temperature for Textile Waste

STAGES	TGA		BTP	
	% Weight	Temp.(⁰ C)	% Weight	Temp.(⁰ C)
1	7	279.2	10	297.4
2	73	363.8	53	521.5
3	18	532.9	10.2	600.5
Residue	2		26.8	

Table 2 shows the comparative decomposition of cotton waste which indicates that in case of first stage the decomposition the weight loss is same while when it comes to TGA and BTP; but in second and third stage the decomposition is lower in case of BTP due to heat transfer losses and also due to the barrier to heat and mass transmission and still at high temperature.

Table 3 - Temperature Range for Different stages of Degradation

Name of Component	Range of Temperature (°C)		
	I st Stage	II nd Stage	III rd Stage
Textile Waste	27.7 – 291	291 - 521.5	521.5 - 600

Table 3 shows the temperature range for three stages of decomposition for textile waste when it comes to TGA and BTP for cotton waste at a heating rate of 10⁰C/min.

Figure 8 - Activation Energy and Frequency Factor for Textile Waste Composition (BTP)

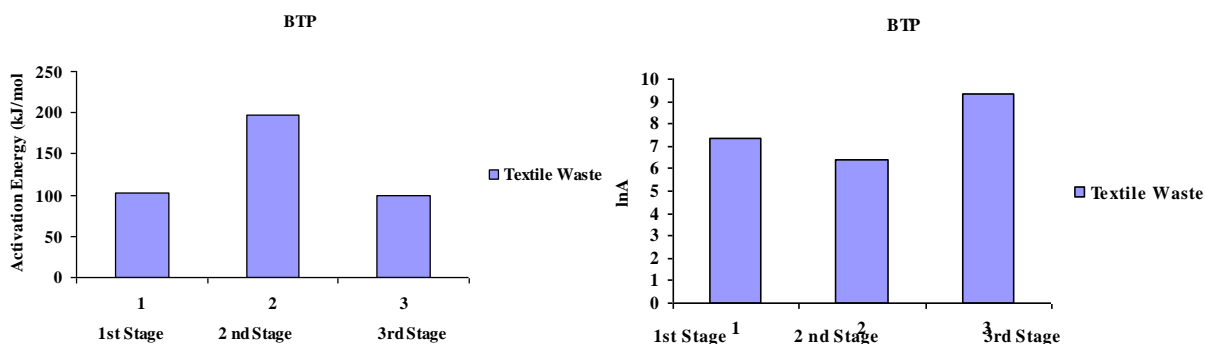


Figure 8 shows the activation energy values for three stages in which compared to first stage, the values of activation energy is higher in second and third stages. During these stages heat can be easily penetrated but in third stage the value of activation energy is low due to less material is available for decomposition. The values of logA increase with rise in temperature.

5. Residues Charactersation

With the assistance of a scanning electron microscope, an elemental analysis of the residual shows the presence of elements at two heating rates of 10 °C/min and 20 °C/min. This elemental analysis also shows influence of heating rates on presence of elements in the residue. Figures 9 and 11 shows the elemental spectrums of cotton residues whereas Figure 10 and 12 shows the photographs of cotton residues at the heating rates of 10 °C/min and 20 °C/min respectively. The further material morphology analysis can also be done and at heating rate 20 °C/min, the fiber of cotton can be clearly seen which shows that at high heating rate, the decomposition does not complete due to lack of heat diffusion to the last cotton fiber. Table 4 represents the effect of heating rates on residues of textile waste composition.

Figure 9 – Elemental Spectrum of Cotton Residues (10 °C/min); Figure 10 – Photograph of Cotton Residues (10 °C/min)

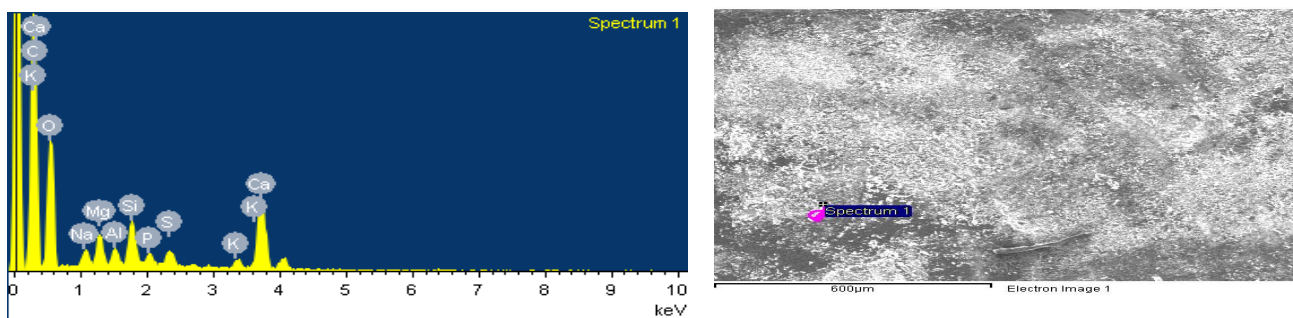


Figure 11 – Elemental Spectrum of Cotton Residues (20 °C/min); Figure 12 – Photograph of Cotton Residues (20 °C/min)

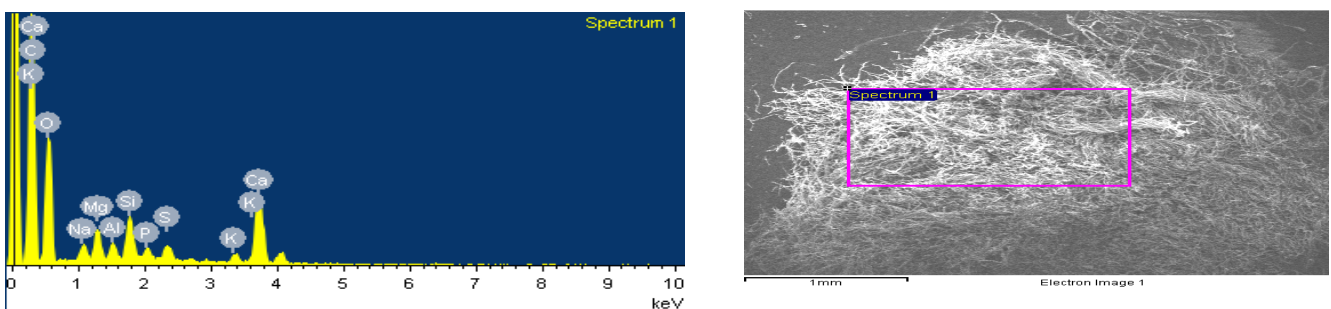


Table 4 - Elements in Cotton Residues

Heating Rate	Element	C	O	Na	Mg	Al	Si	P	S	K	Ca	Total
10 °C/min	Weight%	44.20	38.12	1.27	1.97	0.84	2.48	0.82	1.10	0.83	8.36	100
20 °C/min	Weight%	66.30	26.77	0.0	0.66	0.0	1.14	0.0	0.61	0.0	4.52	100

6. Conclusion

Following major conclusion are drawn from following research work.

1. The heating rate is highly influencing factor in case of decomposition of cotton waste composition.
2. The activation energy is maximum in second stage and rate of decomposition is high in case of heating rate 20 °C/ min.
3. In case of TGA as well as BTP, decomposition occurs in three stages only. But both curves don't superimpose, it may be because of due to heat and mass transfer resistance in case of BTP.
4. In case of SEM, at high heating rate (20 °C/min) less heat is penetrated due to short time period. The decomposition of cotton does not occur properly which and so fibers are seen in SEM results.

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