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Determination of Activation Energy from Pyrolysis of Paper Cup Waste Using Thermogravimetric Analysis

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Abstract

Paper cups waste represents a valuable source of energy. Therefore, it is studied to determine the quantity of energy obtained from waste of known amount and composition. For a waste to become an energy system, the kinetic parameter of waste is one of the important characteristics that determine the energy obtainable from wastes. TGA has frequently been employed in the kinetic study of the thermal degradation of cellulosic materials. In this work, we have studied the thermo gravimetric analysis of paper cup waste at 2 °C/min, 30°C/min in the air and 30 °C/min in the nitrogen atmosphere and determine the activation energy by using thermogravimetric curves. The Activation energy increases from 17 KJ/mol to 28 KJ/mol with increasing heating rate from 25°C/min to 30°C/min in the air atmosphere. Activation energy is less 22 KJ/mol in nitrogen atmosphere as compared to 28 KJ/mol in air atmosphere at a heating rate of 30°C/min.

Keywords: Activation energy, paper cup waste, reaction kinetics, thermogravimetric analysis.

Introduction

Paper cups used as coffee cups or for cold drinks are accumulating as wastes on the earth surface at a rapid rate. Considering only America, 14.4 million disposable paper cups are used for drinking coffee each year. Placed end-to-end, these cups would wrap around earth 55 times and weigh around 900 million pounds. Most paper cups are designed for a single use and then disposed or recycled. A comparison between paper and plastic cups show environmental effects of both with no clear winner. One paper cup represents 4.1g equivalent petrol with a production cost 2.5 times higher than plastic cups. Paper cups are not specifically recycled. They come under regular waste and burnt or put on landfills. Recycling paper cups is difficult because of its composition as a complex of paper and paraffin. Hence they need about 150 years (same as plastics) to degrade because of their plastic foil[1]. The paper cups are produced from wood pulp (cellulose) and polyethylene plastic film, made out of petrol or paraffins, to improve its water resistivity and resistance to heat. Cellulosic resources are in general very widespread and plenty available. As they are not consumed by humans, their cost is relatively low. Some examples are – paper, cardboard, wood, fibrous plant material etc. Cellulosic materials are comprised of lignin, hemicelluloses, and cellulose and are thus called lingo-cellulosic feed stocks. These structural characteristics along with the encapsulation by lignin make cellulosic materials more difficult to hydrolyze than starchy material[2]. Paper and cardboard make up over 40% of the solid waste buried in North American landfills. Of that 40%, a disproportionate amount is attributable to disposable coffee cups. Unlike newspaper and cardboard boxes, disposable paper cups are not recyclable. The thin lining that makes a paper cup waterproof also keeps it from being recycled. All of those cups end up in the nation's landfills[3].

In the view of the important role pyrolysis plays in combustion processes and due to the tremendous diversity of cellulosic biomass feedstocks, a great need exists for robust, comprehensive cellulosic biomass pyrolysis models that could predict product speciation and yields as function of feedstock characteristics and process conditions[4]. Pyrolysis kinetics analysis is one of the most important tools for the description of the effect of process parameters on the feedstock conversion process[5]. Thermo analytical techniques, in particular thermogravimetry (TGA) and derivative thermogravimetry (DTG) allow pyrolysis kinetics to be obtained in a simple and rapid manner. Wu[6] studied kinetics and pyrolysis of mixture of four types of papers (uncoated and coated printing paper, newsprint and tissue paper) for heating rates 1, 2, 5 K/min and results indicated that decomposition occurred in two stages. C. David[7] discussed pyrolysis phenomenon on the basis of a series of TGA experiments for glossy paper also determined kinetics parameters for cardboard. A. N. Garcia[8] obtained the kinetic parameters of the primary reactions of MSW pyrolysis also studied theoretical analysis of the heating rate and heat transfer influences on the biomass decomposition in TG and Pyroprobe. JIN [9] developed a new kinetic model considering the number of weight loss stages equal to the number of reactions. Wu[10] studied pyrolysis of newspaper with TGA system at a constant heating rate of 5 K min^{-1} in nitrogen environment and analyzed pyrolysis products. The residues were analyzed using GC and an elemental analyzer both. Bhuiyan[11] reported TGA studies for newspaper with heating rates 5, 10, 20 K/min for kinetic study and also carried out pyrolysis of newspaper waste. F. Pinto[12] reported the pyrolysis of biomass and effect of plastic waste on slow pyrolysis process and influence of parameters like reaction time and reaction temperature on yield products. Kuen-Song Lin[13] aimed of this work was to obtain pyrolysis and kinetics of RDF and to understand the role of its components on its pyrolysis behavior. Preliminary pyrolysis kinetics of RDF was investigated using a thermo gravimetric analyzer.

In present work, the thermogravimetric analysis of the paper cups waste at heating rate of 25 ºC/min, 30 ºC/min in the air and 30 ºC/min in the N_2 atmosphere has been studied and the kinetic parameter (activation energy) is determined by using thermogravimetric curves. The Activation energy increases from 17 KJ/mol to 28 KJ/mol with increasing heating rate from 25 °C/min to 30 °C/min in the air atmosphere. Activation energy is less 22 KJ/mol in nitrogen atmosphere as compared to 28 KJ/mol in air atmosphere at the heating rate 30 °C/min.

Kinetic Study of Reaction: Thermo gravimetric analysis (TGA) is one of the most commonly used methods to study the kinetics of thermal decomposition reactions. Kinetic analysis of a process can provide information on effect of process parameters on feedstock conversion. Researchers, Ahmaruzzaman and Sharma[14], Hirata[15], Parekh and Rotliwala[16], Parikh and Rotliwala[17], Ramiah (1970)[18] have investigated biomass pyrolysis and found that it can be modeled like a cellulose pyrolysis but since it contains polymers of cellulose, hemi cellulose and lignin so it may vary according to biochemical composition. It has also been stated that pyrolysis cracking can be modeled as 1st order rate equation as:

$$A_{Solids} \rightarrow B_{Solid} + C_{Volatiles} \quad (1)$$

For 1st order reaction, we have:

$$\frac{dx}{dt} = K(1 - x) \quad (2)$$

Where,

$$K = K_o * e^{\left(\frac{-E}{RT}\right)} \quad \text{and} \quad x = \frac{(w_i - w)}{(w_i - w_f)} \quad (3)$$

So,

$$\frac{dx}{dt} = K_o * e^{\left(\frac{-E}{RT}\right)} * (1 - x) \quad (4)$$

Taking heating rate (β) into account;

$$\frac{dx}{dT} * \beta = K_o * e^{\left(\frac{-E}{RT}\right)} * (1 - x) \quad (5)$$

Now taking care of effect of variation of temperature on conversion (x), the following equation has been modeled to represent the pyrolysis reaction:

$$\ln(-\ln(1 - x)) = \ln\left(\left(\frac{K_o R T^2}{\beta E}\right)\right) - \left(\frac{E}{RT}\right) \quad (6)$$

Activation energy (E) for the reaction is obtained by plotting ln(-ln(1-x)) versus 1/T using TGA data for each of the three runs as shown in figure 3. As it can be observed that it is a linear plot thus the slope of this plot gives activation energy for each case as shown in table 2.

Material and Methods

Raw Material: The paper cups waste used in the experiment was collected from NIT campus area in Rourkela, Orissa, India. The cups were cut into small square shaped pieces (about 1 cm side), before use so as to minimize voids inside the reactor as well as to fill maximum amount of material into the reactor.

Characterization of Raw Material: The paper cups waste was analyzed in order to observe the change in the properties of the solid material as a result of pyrolysis.

Proximate Analysis: It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. It was carried out using *ASTM D3172 - 07a* method.

Ultimate Analysis: Ultimate analysis is performed to determine the elemental composition of the material. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of these compositions is subtracted from 100, it gives oxygen percentage composition.

Calorific Value: Calorific value of a material is the amount of heat liberated when 1Kg of that material is burnt. It was determined for paper cups waste using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

Thermo-Gravimetric Analysis: Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the paper cups waste has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample material was done using a DTG60 instrument. In air medium, 4.4 mg of sample was taken and in nitrogen medium, around 5.88 mg of sample was taken and heated up to a final temperature of 700 °C and a residence time of 1 minute at 700 °C was allowed. TGA was performed both in air and nitrogen atmospheres at the heating rates of 25 °C/min and 30 °C/min in air medium and 30 °C/min in nitrogen medium. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of paper cups waste takes place.

Results and Discussion

Characterization of paper cup waste: Proximate analysis is the quickest and simplest way of investigating the fuel quality of solid materials. The proximate analysis and ultimate analysis of paper cup waste is shown in table 1.

Negligible moisture content of paper cup indicates negligible effect on the conversion efficiency and the heating value of the cellulosic biomass; low ash content also indicates less impact on the heating value of paper cup; volatile matter is not very high whereas the high percentage of fixed carbon owes to its cellulosic nature. These properties make paper cup an efficient raw material for good quality fuel.

Table 1
Characterization of paper cup waste

	Paper cup waste
Proximate Analysis (wt%)	
Moisture content	0
Volatile Matter	52
Ash content	2
Fixed carbon	46
Ultimate Analysis (wt%)	
C	46.7
H	6.7
N	2.12
S	0
O	44.4
C/H Molar Ratio	0.57
C/O Molar Ratio	1.4
Empirical Formula	$C_{1.4}H_{2.41}N_{0.05}O$
Gross Calorific Value(MJ/Kg)	20.102

Thermo-Gravimetric Analysis and DTG analysis: The TGA curve figure 1 showed that the maximum thermal degradation of the paper cup took place in the temperature range of 300-400 °C in all the three observations. In nitrogen medium, a second temperature range of 450-500°C is observed for thermal degradation of the paper cup but the vapors obtained during this phase are generally higher hydrocarbons and are non-condensable. Differential thermogravimetry (DTG) curve figure 2 for paper cup waste shows the normalized weight loss rates (-dx/dt) of the waste samples at the heating rates of 25°C/min and 30°C/min in the air atmosphere and 30°C/min in the N_2 atmosphere. The weight loss started at 300-400°C and terminated around 500°C. The maximum weight loss occurred at 365°C, 371°C and 380°C at the heating rates of 25°C/min, 30°C/min in air medium and 30°C/min in N_2 medium respectively. Therefore, the pyrolysis temperature is higher in case of nitrogen atmosphere as compared to air atmosphere. Hence, the 300-500°C range was selected for kinetic evaluation. The level of a considerable weight loss rate was achieved above 300°C. The slow, flat tailing of -dx/dt peak in the upper part of the T domain was considered less interesting than the main decomposition steps. These results also represent that with increase in heating rate the weight loss also increase and corresponding peak temperature also increase. This may be because of delayed decomposition which diffuses more heat in the sample for short time. The results show similar trend and values as reported by L. Sorum[19].

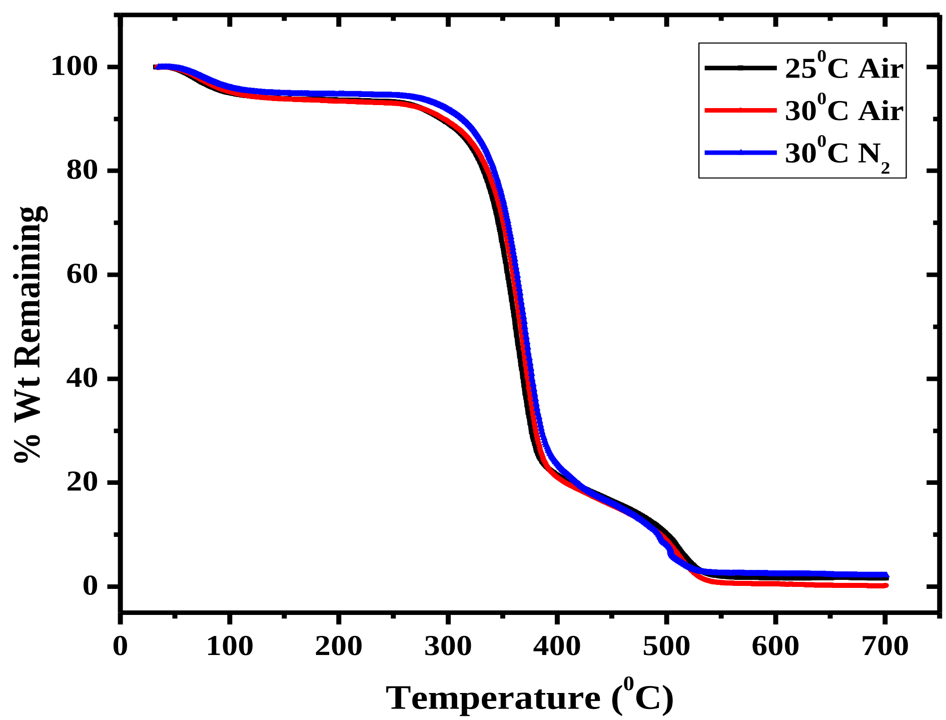

Figure-1
TGA curve of paper cup waste at different heating rates

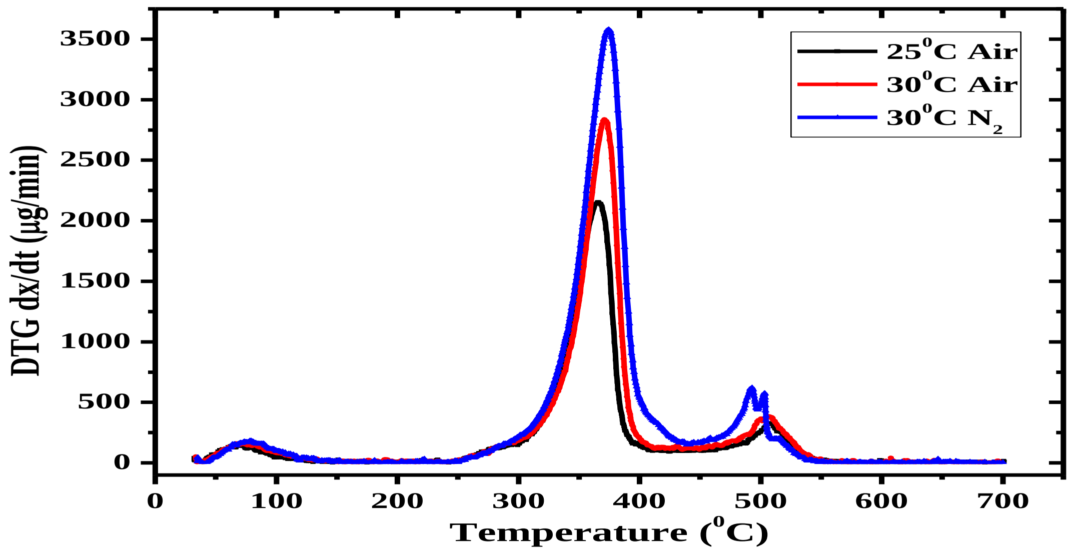

Figure-2
DTG curve of paper cup waste at different heating rates

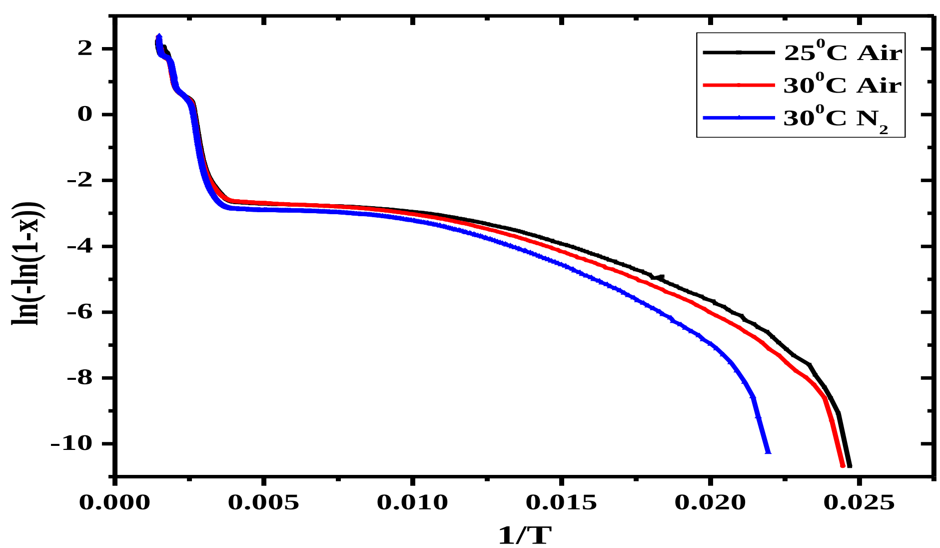

Figure-3
Kinetic Analysis Plot for determination of activation energy of paper cup waste

Table 2
Activation energy for pyrolysis of paper cup waste

	Activation Energy (KJ/mol)		
Sample	**1st Phase**	**2nd Phase**	**3rd Phase**
N_2 30degree/min	22.896756	1.65706334	19.5470454
Air 30degree/min	28.2376696	1.64725282	18.2808232
Air 25degree/min	17.633994	1.3639117	18.0355602

Table 3
Activation energy for various cellulosic biomass feedstocks [21]

Biomass Feedstock	Activation Energy E (KJ/mol)
Corn Stalk	66.518
Wheat straw	70.516
Cotton stalk	71.055
Tree skin	77.316
Wood chip	85.393
Peanut shell	84.47
Seed shell	91.462
Cotton	200.9
Filter paper	227.296

The pyrolysis temperature range for most of the cellulosic feedstocks lies in the range of 300-400°C, such as 311.2°C-338.3°C for glossy paper waste[20]. Similarly, for the temperature range at which maximum thermal degradation took place was found out to be 359°C-387°C for newspaper[11]. The maximum rate of weight losses between 355°C-371°C for pyrolysis of the cellulosic fraction in municipal solid wastes[19].

Kinetic study by the thermo gravimetric analysis: Pyrolysis kinetic analysis is valuable for the in-depth exploration of process mechanisms. On the basis of thermo gravimetric analysis of different kinds of cellulosic biomass feedstocks, thermal kinetics analysis was performed to analyze the pyrolysis behavior of paper cups waste. With the apparent kinetic parameters derived, a kinetic model was proposed for the main reaction section of cellulosic biomass pyrolysis process. figure 3 shows the plot between ln(-ln(1-x)) and 1/T. Reactions having less activation energy take place much easily than reaction with high activation energy. table 2 shows the activation energies of three phases of degradation during thermal pyrolysis of paper cup waste. Activation energy increases from 17 KJ/mol to 28 KJ/mol with increasing heating rate from 25°C/min to 30 °C/min in the air atmosphere. Activation energy is less 22 KJ/mol in nitrogen atmosphere as compared to 28 KJ/mol in air atmosphere at the heating rate 30°C/min. Comparing the activation energy for pyrolysis of paper cup waste with activation energies of other cellulosic biomass feedstocks (table 3), the value is relatively very small. Hence paper cup can be used as a blend in the pyrolysis of feedstock having higher activation energy for their easier thermal degradation.

Conclusion

The thermogravimetric study helps to interpret physical and chemical properties and the thermal behavior of the given type of cellulosic feedstock. Determining the kinetic parameters also provides information to design more effective conversion systems and optimum pyrolysis regimes. Activation energy increases with increasing heating rate of pyrolysis in the air atmosphere. Activation energy is more in air atmosphere as compared to nitrogen atmosphere at the heating rate of 30°C/min. Activation energy of the pyrolysis of paper cup waste was found out to be in lower range thus enabling it to be used as a blend for easy pyrolysis of materials with higher activation energy.

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