

Kinetic Parameter Estimation of Cotton Polyethylene Mixture

Samit Kumar Singh¹ and Dr. Sadanand A. Namjoshi²

¹Research Scholar, Madhav University, Pindwara (Sirohi) – 307026, Rajasthan, India

²Professor, Madhav University, Pindwara (Sirohi) – 307026, Rajasthan, India

E-mail: samit.meet@gmail.com¹

ABSTRACT

The energy crisis and greenhouse emissions are two major issues at the minute. Plastic waste dumped in landfills is also a big problem because the decomposition rate is almost 500 years or more. Pyrolysis, incineration, and gasification are examples of thermal oxidation processes that can be used to optimize waste upgrade. Conversely, thermal degradation of polymer mixtures at varying temperatures enables the polymer to degrade at a quicker rate. The appropriate design of a reactor for the decomposition of waste plastic and other municipal solid (MSW) constituents and the extraction of fuel either in solid, liquid, or gaseous form plays an important role. Any pyrolysis reactor's efficient design is based on kinetic knowledge. Thermogravimetric analysis (TGA) is a widely accepted technique for estimation of kinetics parameters. The current work consists of TG/DTG results for cotton (textile waste), polyethylene, and a mixture of polyethylene textile materials with heating rates (β) of 5, 10, and 20 °C/min using the TG differential system balance mechanism in a nitrogen atmosphere for kinetics parameter estimation; and ash analysis of samples at the mentioned heating rates using a scanning electron microscope for investigation of various elements in the ash. Kinetic parameters and SEM results are not available in the open literature, which is the core area of research.

Keywords: Thermo-gravimetric Analysis, Polyethylene, Scanning Electron Microscope.

1. INTRODUCTION

Waste generation is due to various human activities, and the way wastes are managed may create risk to the atmosphere and to public wellness. Management of solid waste and disposal is most challenging task for urban and industrial areas in present scenario. Solid waste handling should ensure the safety of human health while considering the promotion of sustainable economic growth. The Municipal Solid Waste (MSW) produced per capita per day in developed countries varies from 0.5 to 2.0 kg while for under developed countries this figure lies on average in the range of 0.4 to 0.8 kg by considering towns to metro cities (Joseph, 2002; Kumar *et al.*, 2009).

Waste-to-Energy is excellent and the promising route for handling large quantity MSW. MSW is heterogeneous in nature and it consists of constituents like paper (printing paper, glossy paper, card board and newspaper), textile waste, biodegradables, food, plastics, metals, rubber, glass and non-combustible. The technologies available on commercial scale for Waste-to-Energy are (1) Sanitary landfill (2) Anaerobic digestion (3) Gasification/Pyrolysis (4) Incineration (5) other types (Kumar *et al.*, 2009; Becidan, 2007; Kumar *et al.*, 2001).

Out of all available technologies pyrolysis is promising one (Becidan, 2007; Kumar *et al.*, 2001) with minimum impact on environment and maximum energy outcome. It (Morcos, 1989) presents various options of energy recovery from MSW while it (Murphy and Mckeogh, 2004) give comparative assessment of four technologies for MSW-to-Energy conversion. The correlation for estimation of HHV is presented by (Kathiravale *et al.*, 2003) based on physical composition of Malaysian MSW. The micro level kinetics studies of MSW constituents have been presented by few researchers while pyrolysis products yield and their analysis have also been reported on the literature by researchers (Garcia *et al.*, 1995; Wu *et al.*, 1997; Sorum *et al.*, 2001; David *et al.*, 2003; Miranda *et al.*, 2007; Bhuiyan *et al.*, 2008; Wu *et al.*, 2002; Encinar and Gonzalez, 2008; Aboulkas *et al.*, 2009).

An overview of MSW generation data and realized that definition of MSW differ throughout world so, there is uncertainty in published data. It is difficult to calculate MSW per capita generation rate for purpose of comparing various countries and region. Though uncertainties can be never eliminated, if correct data is available, then it helps to find true picture of socio-economic growth, future MSW generation projection and impact of selected technology on environment (Kawai and Tasaki, 2016). It is also reviewed that kinetics of pyrolysis for treatment of MSW and concluded that pyrolysis is best suitable thermo chemical technology. Problem lies in scaling up the pyrolysis technique and also discussed various analytical techniques available for characterization of sample as well as residual oil, gas and ash (Chhabra *et al.*, 2016). Its already postulated that bed density and pyrolyser pressure resist the vapor movement through the bed. The formation of vapor's (gaseous longer chain) and gaseous (short chain) compounds and the percentage of recondensation reactions taking place are influenced by these factors.

An extended duration of the vapors within the pyrolyser reactor will result in further side reactions to take place and this can result into lower oil yields and more charcoal yield (De Jongh, 2001). It used a two-stage method to produce hydrogen from waste plastics through catalytic steam pyrolysis–gasification. The effect of three main parameters, namely the catalyst to plastic ratio, gasifying temperature, and water injection rate, on the output of hydrogen using real-world plastic wastes extracted from municipal solid waste, was examined (Wu and Williams, 2010).

The pyrolysis of newspaper was investigated at temperatures ranging from 573 to 1173 degrees Fahrenheit. These pyrolysis product properties can be used as a starting point for designing a pyrolysis method for biomass wastes. The method has been mathematically modelled in a deterministic manner, taking into account the phenomenon of deactivation (Sarkar *et al.*, 2015).

To understand pyrolysis and degradation behavior of different MSW constituents and for controlling the process, knowledge of kinetics parameters related to the process is essential. The present work related to thermal decomposition characteristic of cotton and polyethylene waste and mixture of both at micro level with sample size of 6 mg using thermogravimetric analysis (TGA) analytical method.

2. EXPERIMENTAL METHODOLOGY

2.1 Material

Cotton waste and polyethylene from waste packaging boxes were used in the tests, which were sliced into tiny 1-2 mm sections. The sample size is limited to the size of the container of the material used in the TGA. Table I reveals Cotton Waste and Polyethylene's proximate, ultimate consequence and HHV.

Table I Proximate Analysis, Ultimate Analysis and Higher Heating Value of Cotton Waste and Polyethylene

[A] Cotton Waste									
Fixed Carbon (% wt)	Volatile Matter (% wt)	Moisture (% wt)	Ash (% wt)	Carbon (% wt)	Hydrogen (% wt)	Nitrogen (% wt)	Sulphur (% wt)	Oxygen (% wt)	HHV MJ/kg
5.7	3.61	89.3	1.39	45.92	6.05	0.12	0.57	45.90	17.87
[B] Polyethylene									
Fixed Carbon (% wt)	Volatile Matter (% wt)	Moisture (% wt)	Ash (% wt)	Carbon (% wt)	Hydrogen (% wt)	Nitrogen (% wt)	Sulphur (% wt)	Oxygen (% wt)	HHV MJ/kg
1.11	0.19	93.83	4.87	80.15	3.99	2.42	0.60	7.96	31.77

2.2 Thermogravimetric Analysis (TGA)

Polysers and gasifiers have a specification that involves a conceptual understanding of the components of MSW kinetics for temperature range and heating speeds. In the TG/DTG system, TGA and DTG were implemented. The temperature range for micro thermal degradation in the nitrogen atmosphere ranges from the temperature of room (RT) to 600 °C for heating rates of 5, 10 and 20 °C /min and the flow rate of gas was 50 ml/min. The size is 6 mg of cotton waste, polyethylene and a combination of cotton waste as well as polyethylene.

3. KINETICS

It is important for MSW to estimate kinetic parameters for understanding the pyrolysis reaction mechanism. The thermal degradation of MSW constituents can be estimated using analytical models (David *et al.*, 2003; Miranda *et al.*, 2007; Wu *et al.*, 2002).

The current model is used to evaluate activation energy (Sorum *et al.*, 2001; David *et al.*, 2003) using TGA data.

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT$$

Here A denotes pre-exponential or frequency factor, β denotes the heating rate, R denotes constant universal gas (8.314 kJ mol⁻¹K⁻¹) and E denotes the activation energy. There is no exact solution to this equation; thus, by the Flynn wall - Ozawa method (Kathiravale *et al.*, 2003), various approximations have been performed for cotton, polyethylene and decomposition combination.

The Flynn wall - Ozawa (Meraz *et al.*, 2003) approach was used for three heating thresholds of activation energy in the case of TGA.

4. RESULTS AND DISCUSSION

A. Cotton Waste (Textile Waste)

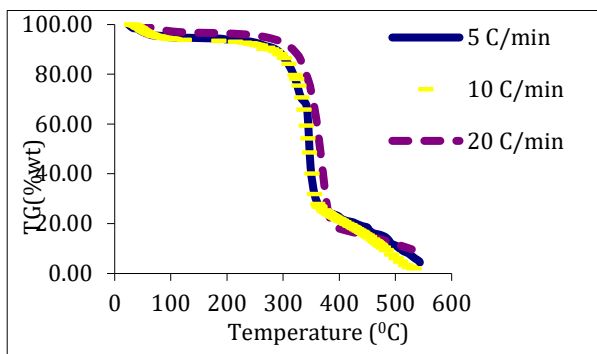


Figure 1 TG Curves

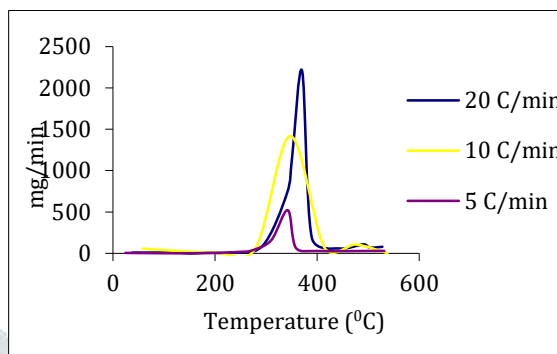


Figure 2 DTG Curves

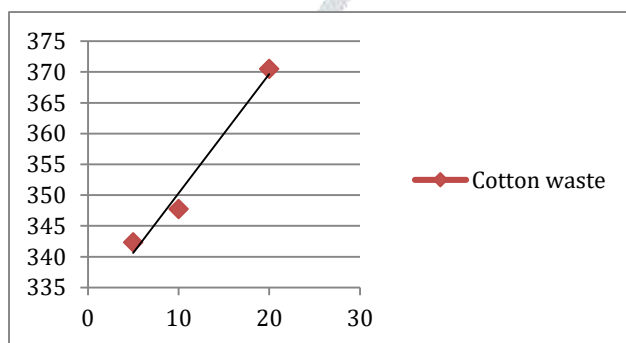


Figure 3 T_{max} Corresponding to DTG_{max} for Cotton Waste

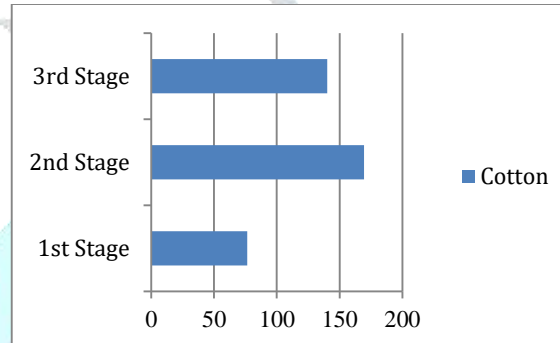


Figure 4 Activation Energy for Cotton Waste

TG curves and DTG curves of cotton waste for heating rates (β) 5, 10 and 20 °C/min are shown in Figure 1 and Figure 2. The highest temperature value for DTG corresponding to varying heating rates is illustrated in Figure 3 and the kinetic constant values for three stages of decomposition are shown in Figure 4.

A three-stage weight loss with respect to temperature is observed from Figure 1 and Figure 2. In first stage, hemicellulose may get decomposed and due to low level of temperature and mass transfer resistance (Garcia *et al.*, 1995; Sorum *et al.*, 2001; David *et al.*, 2003; Bhuiyan *et al.*, 2008), the degradation rate is slow. In second stage decomposition of cellulose and in third stage of lignin take place, respectively, except in case of textile waste wherein third stage synthetic materials get decomposed. Observations similar to these are stated by (Miranda *et al.*, 2007) and which strengthen the current work.

The losing weight increases at a higher rate in all three phases with increases in heating rate as the heating rate improves kinetics. On the DTG curves, the three main peaks that contribute to the three-stage weight loss on a TG curves can be seen. In the case of three stages, the peak value of the activation energy is confirmed to be at the second level. The main stage of decomposition is found to be in the second stage, which has a high activation energy. In the third level, the activation energy is lower due to a low degradation rate. The rate of decomposition is observed to increase with an increase in the rate of heating and lowers in the overall amount of decomposition. This could be attributed to a lack of degradation period with rising heating rates for the reaction to complete (David *et al.*, 2003; Bhuiyan *et al.*, 2008). In the case of cotton waste, the main weight loss for temperatures ranging from 240-400 °C occurs in the second level which is also described (Sorum *et al.*, 2001).

B. Polyethylene (Polymer)

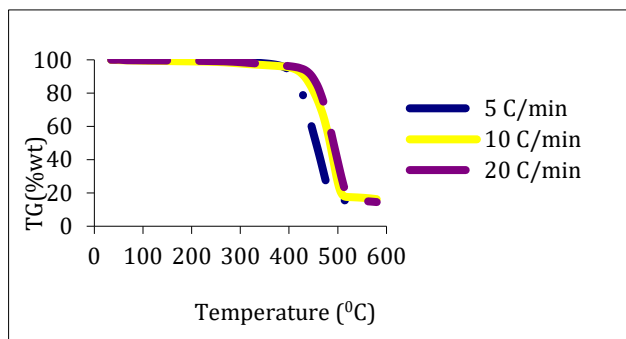


Figure 5 TG Curves

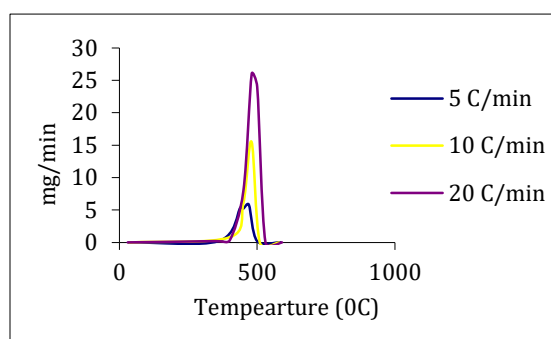


Figure 6 DTG Curves

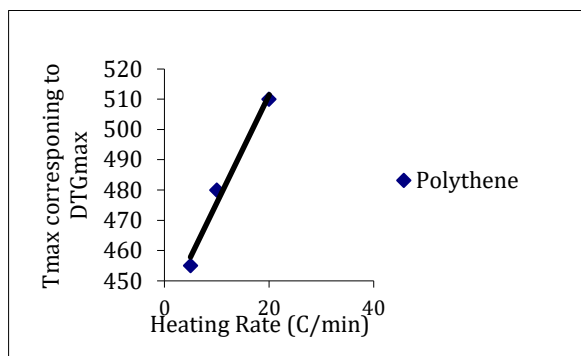


Figure 7 T_{max} Corresponding to DTG_{max}

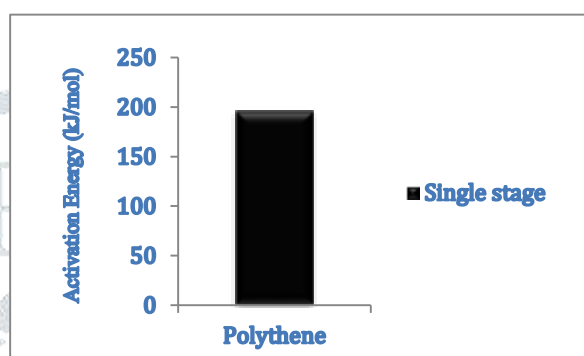


Figure 8 Activation Energy

Figure 5 and Figure 6 represents the loss in weight characteristics and DTG curves of polyethylene at heating rates (β) 5, 10, 20 °C/min. It is interesting to observe from these results that the degradation occurs in single stage as also reported by (Sorum *et al.*, 2001) and corresponding temperature ranges are 395-525°C for polyethylene. Figure 5 and Figure 6 indicates that in case of polyethylene, the decomposition occurs at faster rate compared to textile waste which may be related to bond energy level (Encinar and Gonzalez, 2008; Aboulkas *et al.*, 2009). The value of kinetic constant increases with increases in degree of transformation and in case of polyethylene the mean values of activation energy is 195.96 kJ/mol. The findings indicate a pattern and values that are close to those identified by (Encinar and Gonzalez, 2008). The decomposition increases with increase in heating rates but residues remain in case of polyethylene is lower compared to textile waste. Figure 7 and Figure 8 represents Maximum Temperature for DTG corresponding to heating rate and activation energy of polyethylene, respectively.

C. Cotton (Textile)- Polyethylene (Polymer)

Experiments on mixture of two components were carried out to understand their interaction. For this purpose, both samples are thoroughly mixed and kept in the crucible for investigation of decomposition behavior (Sorum *et al.*, 2001; Encinar and Gonzalez, 2008). There are no TG/DTG research for cotton-polymer mixtures in the open literature and the attempt has been made to understand decomposition behavior of such composition.

Figure 9 and Figure 10 represent the TG curves and DTG curves for cotton–polyethylene mixtures for three heating rates as (β) 5, 10 and 20 °C/min, respectively, while Figure 11 shows values of kinetic constants and Figure 12 indicates the maximum temperature corresponding to maximum decomposition rate, respectively.

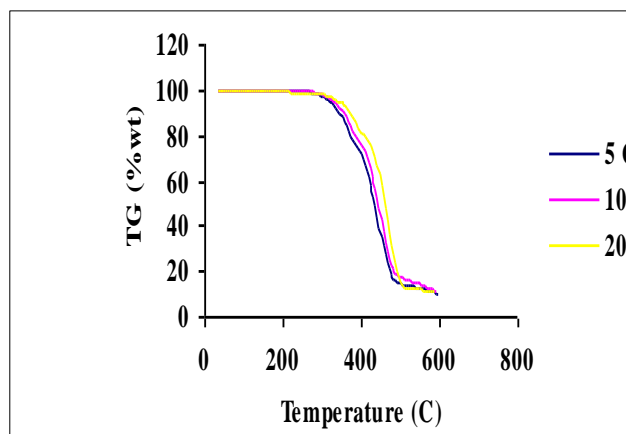


Figure 9 TG Curves

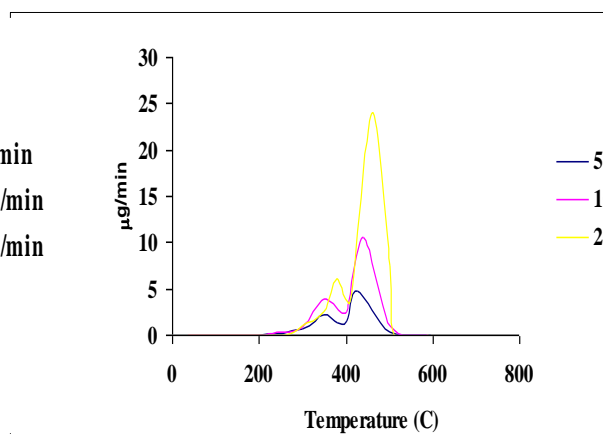


Figure 10 DTG Curve

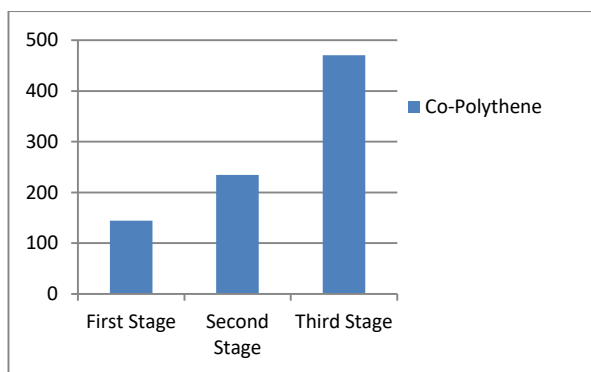
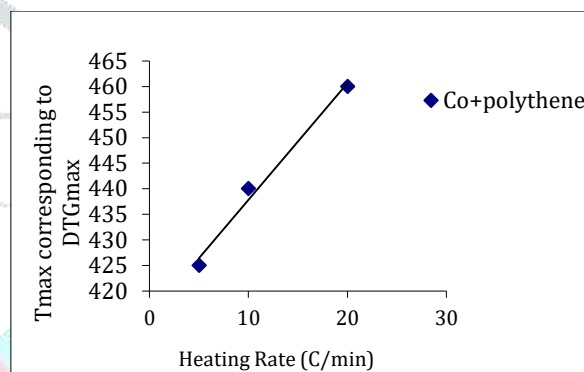


Figure 11 Activation Energy

Figure 12 T_{max} Corresponding to DTG_{max}

In case of cotton – polythene composition thermal decomposition is observed at faster rate for all heating rates compared to other cotton-polymer composition while in case of cotton-pvc, decomposition is observed at a slower rate and more residue remain after each cycle. In case of cotton-polymer composition decomposition of cotton occurs in three stages (Sorun *et al.*, 2001; Encinar and Gonzalez, 2008; Aboulkas *et al.*, 2009). The two major decompositions occur in temperature range of 320- 420 °C and 420- 490 °C.

It should be remembered that the temperature of the mixture varies only marginally compared to the mixture temperature range for each component. It is found that in the case of plastics, the residue remains large compared with the mixture after decomposition. This may be due to the existence of two distinct classes of components of MSW that affect the decomposition of each other. At lower temperatures than pure plastics, plastics in a blend degrade while cotton in a mix degrades faster than plain cotton at higher temperatures. Co-components exhibit a distinct behavior from that of the pure materials in all mixtures. A substantial relationship is discovered in the third stage of decay, though the first two phases are unchanged. The third stage's major involvement is most definitely due to the fact that as observed by (Aboulkas *et al.*, 2009), the products produced during the degradation of cotton residue can influence the processes of plastic degradation.

CONCLUSIONS

A. Cotton Waste

The activation energy for the 5 °C/min to 20 °C/min heating rate is 76.46 kJ/mol in the first phase, 169.53 kJ/mol in the second phase and 140.09 kJ/mol in the third phase correspondingly for textile waste.

B. Polyethylene Waste

The activation energy corresponding to heating rate of 5 °C/min to 20 °C/min is 195.96 kJ/mol, 160.98 kJ/mol and 212.26 kJ/mol for polyethylene.

C. Cotton - Polyethylene Composition

In case of all textile-polymer compositions, the decomposition occurs in three stages.

The activation energy in phases first, second and third of cotton-polyethylene waste for the heating rates of 5 °C/min, 10 °C/min and 20 °C/min is obtained as 144.64 kJ/mol, 234.59 kJ/mol and 470.24 kJ/mol correspondingly.

The activation energy in first, second and third stage for cotton – polystyrene waste for the heating rates of 5 °C/min, 10 °C/min and 20 °C/min is observed to be 280.6 kJ/mol, 252.79 kJ/mol and 280.36 kJ/mol, respectively.

REFERENCES

- Aboulkas, A., El harfi, K., El bouadili, A., Nadifiyine, M., Benchanaa, M. and Mokhlisse, A. (2009), “Pyrolysis kinetics of olive residue/plastic mixtures by non-isothermal thermogravimetry”, *Fuel Processing Technology*, Vol. 90 No. 5, pp. 722-728.
- Becidan, M. (2007), “Experimental Studies on Municipal Solid Waste and Biomass Pyrolysis”, Thesis for the degree of doctor philosophy.
- Bhuiyan, M.N.A., Murakami, K. and OTA, M. (2008), “On Thermal Stability and Chemical Kinetics of Waste Newspaper by Thermogravimetric and Pyrolysis Analysis”, *Journal of Environment and Engineering*, Vol. 3 No. 1, pp. 1-12.
- Chhabra, V., Shastri, Y. and Bhattacharya, S. (2016), “Kinetics of pyrolysis of mixed municipal solid waste-A review,” *Procedia Environmental Sciences*, Vol. 35, pp. 513-527.
- Chunfei, Wu. and Williams, P. T. (2010), “Pyrolysis–gasification of post-consumer municipal solid plastic waste for hydrogen production”, *International Journal of Hydrogen Energy*, Vol. 35, pp. 949-957.
- David, C., Salvador, S., Dirion, J.L. and Quintard, M. (2003), “Determination of a reaction scheme for cardboard thermal degradation using thermal gravimetric analysis”, *Journal of Analytical and Applied Pyrolysis*, Vol. 67 No. 2, pp. 307-323.
- De Jongh, W. A. (2001), “Possible Applications for Vacuum Pyrolysis in the Processing of Waste Materials,” PhD Thesis, Stellenbosch: Stellenbosch University.
- Encinar, J.M. and González, J.F. (2008), “Pyrolysis of synthetic polymers and plastic wastes. Kinetic study”, *Fuel Processing Technology*, Vol. 89 No. 7, pp. 678-686.
- Flynn, J.H. and Wall, L.A. (1966), “A quick, direct method for the determination of activation energy from thermogravimetric data”, *Journal of Polymer Science Part B: Polymer Letters*, Vol. 4, pp. 323-328.
- Garcia, A.N., Marcilla, A. and Font, R. (1995), “Thermogravimetric kinetic study of the pyrolysis of municipal solid waste”, *Thermochemica Acta*, Vol. 254, pp. 277-304.
- Joseph, K. (2002), “Perspectives of solid waste management in India”, *International Symposium on the Technology and Management of the treatment & Reuse of the Municipal Solid Waste*, Shanghai, China, pp. 1-14.
- Kathiravale, S., Muhd Noor Muhd Yunus., Sopian, K., Samsuddin, A.H. and Rahman, R.A. (2003), “Modeling the heating value of Municipal Solid Waste”, *Fuel*, Vol. 82 No. 9, pp. 1119-1125.
- Kawai, K. and Tasaki, T. (2016), “Revisiting estimates of municipal solid waste generation per capita and their reliability,” *Journal of Material Cycles and Waste Management*, Vol.18 No. 1, pp.1-13.
- Kumar, J.S., Subbaiah, K.V. and Prasada Rao, P.V.V. (2001), “Municipal Solid Waste Management Scenario in India”, *Australian Journal of Engineering Research, SCIE Journals*, TERI Information Monitor on Environmental Science, Vol. 6, pp. 1-8.
- Kumar, S., Bhattacharyya, J.K., Vaidya, A.N., Chakrabarti, T., Devotta, S. and Akolkar, A.B. (2009), “Assessment of the status of municipal solid waste management in metro cities, state capitals, class I cities, and class II towns in India: An insight”, *Waste Management*, Vol. 29 No. 2, pp. 883-895.
- Meraz, L., Dominguez, A., Kornhauser, I. and Rojas, F. (2003), “A thermo chemical concept-based equation to estimate waste combustion enthalpy from elemental composition”, *Fuel*, Vol. 82 No. 12, pp. 1499-1507.
- Miranda, R., Sosa_Blanco, C., Bustos-Martinez, D. and Vasile, C. (2007), “Pyrolysis of textile wastes: I. Kinetics and yields”, *Journal of Analytical and Applied Pyrolysis*, Vol. 80 No. 2, pp. 489-495.
- Morcós, V.H. (1989), “Energy recovery from municipal solid waste incineration - A review”, *Heat Recovery Systems and CHP*, Vol. 9 No. 2, pp. 115-126.
- Murphy, J.D. and McKeogh, E. (2004), “Technical, economic and environmental analysis of energy production from municipal solid waste”, *Renewable Energy*, Vol. 29 No. 7, pp. 1043-1057.

Sarkar, A., Sarkar, S. D., Langanki, M. and Chowdhury, R. (2015), “Studies on pyrolysis kinetic of newspaper wastes in a packed bed reactor: Experiments, Modeling, and Product Characterization”, *Hindawi Publishing Corporation Journal of Energy*, Vol. 2015, Article ID 618940, 8 pages.

Sorum, L., Gronli, M.G. and Hustad, J.E. (2001), “Pyrolysis characteristics and kinetics of municipal solid wastes”, *Fuel*, Vol. 80 No. 9, pp. 1217-1227.

Wu, Chao-Hsiung., Chang, Ching-Yuan., Lin, Jyh-Ping. and Hwang, Jiann- Yuan. (1997), “Thermal treatment of coated printing and writing paper in MSW: pyrolysis kinetics”, *Fuel*, Vol. 76 No. 12, pp. 1151-1157.

Wu, Chao-Hsiung., Chang, Ching-Yuan. and Tseng, Chao-Heng. (2002), “Pyrolysis products of uncoated printing and writing paper of MSW”, *Fuel*, Vol. 81 No. 6, pp. 719-725.

