Modh J.K, Namjoshi S.A, Channiwala S.A / International Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622 www.ijera.com
Vol. 2, Issue 2,Mar-Apr 2012, pp.1067-1074

Kinetics and Pyrolysis of Glossy Paper Waste

Modh J.K*, Namjoshi S.A, Channiwala S.A****
*(Department of Mechanical Engineering, U.V Patel Engineering Collage)
** (Department of Mechanical Engineering, Sadrdar Vallabhbhai National Institute of Technology, Surat)

Abstract

Energy consumption, waste generation and greenhouse gas emissions will continue to grow as long as population and economic growth persists. These are serious challenges to the global community. The ever increasing quantity of Municipal Solid Waste (MSW) generated in the modern world has posed several social and health problems. The aim of present work is to carry out thermogravimetric analysis of glossy paper (TGA) at heating rates (β) 5,7,10,15,20 ^{0}C/min using TG/DTG 32 horizontal differential system balance mechanism. The weight loss occurs in three stages and which might be associated with lignin, cellulose and hemicellulose respectively. The temperature ranges from room temperature (RT) to 274 ^{0}C, 274 ^{0}C - 361 ^{0}C and 361 ^{0}C- 542 ^{0}C in all three stages with average weight loss of 60 %. The pyrolysis of glossy paper is also carried out using Batch type Pyrolyser (BTP) and product yields which obtained are analyzed using analytical methods like Gas chromatography, Mass spectroscopy Gas chromatography and scanning electron microscope.

Keywords: Gas chromatography, Glossy paper, Kinetics, Pyrolysis, Thermogravimetric analysis,

1.Introduction

Global warming and diminishing energy supplies are two major current concerns and solution of this is Municipal Solid waste (MSW). The energy-to-waste is the only solution of present scenario and the options are land filling, incineration, pyrolysis and gasification of MSW; out of which land filling and incineration having adverse impact on environment and so pyrolysis is preferably good option, which is a significant and growing problem in many urban areas of the developing world [1,2,3,4]. Current systems of waste management in most developing country cities are very rudimentary at best and are grossly inefficient and ineffective. The Asian countries where two third of the total population of the world are becoming garbage because of improvement in life style, modernization and high GDP [1,2]. It is observed that the generation rate ranges from 0.3 to 1.0 kg/capita/day [5, 6]. The country like India where the GDP is more than 7 % the waste management is becoming severe issues and the waste consists of about 7-9 % [1,5,6] of paper waste and one the major constituents is glossy paper and so handling of such waste-to-energy challenging task.

A.N. Garcia [7] 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. C. David [8] discussed pyrolysis phenomenon on the basis of a series of TGA experiments for glossy paper also determined kinetics parameters for cardboard.Wu [9] 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. Sørum [10] has also studied degradation of four types of papers and five different plastics at heating rate of 10^{0}C/min. The results indicate that the degradation of papers occurred in three stages while decomposition of plastic occurs in single stage except poly vinyl chloride, considering single reaction model with parallel and independent reactions. JIN[11] developed a new kinetic model considering the number of weight loss stages equal to the number of reactions. Wu [12] studied pyrolysis of newspaper with TGA system at a constant heating rate of 5 K min^{-1} in nitrogen environment and analysed pyrolysis products. The residues were analyzed using GC and an elemental analyser both. Bhuiyan[13] 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 [14] 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 [15] 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. Ch. Pasel[16] focused on pyrolysis of shredder waste as a possible way for chemical recycling of plastic wastes and deals with the technical requirements for an industrial application. S. Ojolo [17] suggested the strength pyrolysis thermo chemically process for converting MSW into fuel and to manage wastes through volume reduction.

The aim of present work is to investigate the degradation behaviour of glossy paper waste for five heating rates (β) 5,7,10,15,20 ^{0}C/min in nitrogen atmosphere with TGA with TGA and estimation of kinetic parameters using Coats- Redfern method [18].

The pyrolysis of glossy paper is carried out at heating rate of 10 ^{0}C/min and yield products are analyzed using existing analytical methods.

Additionally, elemental analysis of residue of glossy paper for heating rate of 10^{0}C/min and 20 10^{0}C/min with scanning electron microscope (JEOL 5610LV) using Energy Dispersive Spectroscopy (EDS) is carried out.

2. Experimentation

2.1 Material

The experiments were carried out on commercial glossy paper which was cut into small pieces of 2-3 mm. The particle size used in BTP is larger compared to TGA due to no weight and size constrains of crucible. Table 1 shows proximate analysis and ultimate analysis result and HHV of glossy paper.

Table 1 Proximate Analysis, Ultimate Analysis and Higher Heating Value

ixed Carbon (% wt)	olatile Matter (% wt)	Ash (% wt)	Carbon (% wt)	Hydrogen (% wt)	Nitrogen (% wt)	Sulfur (% wt)	xygen % wt)	HV J/kg
5.18	68.51	26.31	64.2	3.39	1.49	0.52	3.43	6.47

2.2 Thermogravimetric Analysis (TGA)

The thermogravimetric and differential thermogravimetric analysis were carried out in SEIKO TG/DTA-32 thermal system. Samples were scanned between room temperature (RT) to 600^{0}C with heating rate of (β) 5, 7,10,15,20 ^{0}C/min in nitrogen gas atmosphere and with 50 ml/min flow rate. The maximum sample size was 6 mg. Samples were placed in platinum crucible and α alumina was used as reference.

2.3 Batch Type Pyrolyser

Pyrolysis of Glossy paper was carried out in Batch Type Pyrolyser (BTP) having PLC control system to obtain different heating rate in temperature range of RT to 1200^{0}C. The concentric tube heat exchanger was used to condense the volatiles produced in the reactor. The nitrogen purging rate was 2 l/min and heating rate was 10^{0}C/min from RT to 600 ^{0}C with sample size approximately 60 gm. Two thermocouples were inserted to measure the temperature of heater as well as temperature of sample.

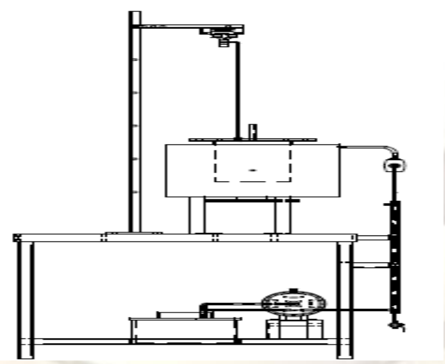


Fig 1 Batch Type Pyrolyser

3. Kinetics

A relatively simple approximation for determining the kinetics of the thermal decomposition consists of assuming the reaction to be first order using Coats- Red fern method [18]. The weight loss or conversion is converted to a normalized form α and is called reaction progress with temperature. For non isothermal TGA the reaction progress is given by

$$\alpha = {(m_0 - m_T)}\big/{(m_0 - m_\delta)} \quad \text{--- (1)}$$

m_T is the sample weight at temperature T, m_0 is the initial weight and m_δ is the final weight of sample.

The Arrhenius parameters, for the thermal decomposition of the samples were determined considering first order chemical reaction [18]. This method uses the integral form of rate law. The rate law of any solid phase reaction can be given as

$$d\alpha/dt = Ae^{-E/RT}(1-\alpha) \text{ --- (2)}$$

In non-isothermal TGA experiments the heating rate is varied as a function of time

$$d\alpha/dt = d\alpha/dt * dt/dT \text{ --- (3)}$$

$$dx/dt = d\alpha/dt * 1/\beta \text{ --- (4)}$$

β is the heating rate given by dT/dt

$$d\alpha/dT = (A/\beta) * e^{-E/RT}(1-\alpha) \text{ --- (5)}$$

A β is the heating rate. Plotting the left hand side against the 1/T gives E/R as the slope and A as the intercept. Assuming the reaction to be of first order and integrating and taking logarithm on both sides we get

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{\mathrm{E}}{\mathrm{RT}}\ \frac{2RT}{E} << 1 \text{ --- (6)}$$

A plot of $\ln[-\ln(1-\alpha)/T^2]$Vs 1/T will give the activation energy and frequency factor.

4. Results AND Discussion

4.1 Kinetics based on TGA

A three stage decomposition weight loss is observed from Figure 2.In first stage hemicellulose, in second and third stage the degradation of cellulose and lignin may take place respectively [7]. Figure 2 reflects the similar TG curves pattern for all the heating rates, however rates are varying. The degradation occurs at a faster rate in second stage compared to first and third stage as heating rate increases. The weight loss increases in all stages at a faster rate with increase in heating rate. The temperature for all three stages was in the range of 28 ^{0}C to 274 ^{0}C, 274 ^{0}C - 361 ^{0}C and 361 ^{0}C- 542 ^{0}C respectively. The weight loss in first, second and third stage were in the order of 6-10 %, 30-34 % and 18-20 % respectively and 39-41 % residue left after experiment was over. Table 2 presents the values of kinetic constants for different heating rates, and it is observed that with increase in heating rate the magnitude of activation energy increases. The reason may be at high heating rate the accessibility of temperature for reaction to occur is high for small period of time and will favor the formation of active molecules and also molecular collision increases. It also indicates that in case of three stages the kinetic constant having maximum value in second stage. It is observed that activation energy increases with increase in heating rate for second stage which is the major stage of decomposition. Activation energy is lower in the third stage due to low degradation rate. Figure 3 represents DTG curves. Corresponding to the three-stage weight loss on the TG curves, three peaks are observed on the DTG curves. It can be observed that as heating rates increase there is a lateral shift towards higher temperatures of DTG curves and which may be due to the combined effects of the heat transfer at different heating rates and the kinetics of the decomposition resulting in delayed decomposition [10].

Table 3 shows the peak value of DTG temperature corresponding to various heating rates. Results represent that with increase in heating rate the weight loss also increase and corresponding peak temperature also increase may be because of delayed decomposition which diffuse more heat in the sample for short time. The results show similar trend and values as reported by L.sorum [10].

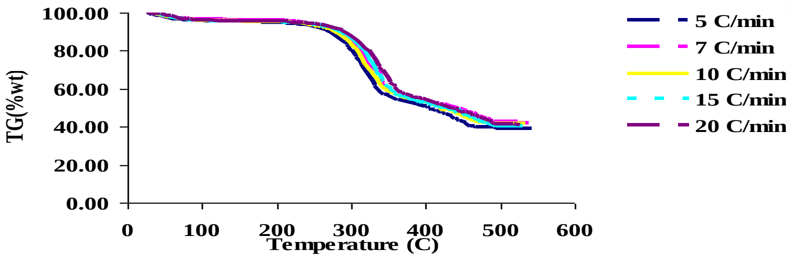


Fig 2 TG Curves

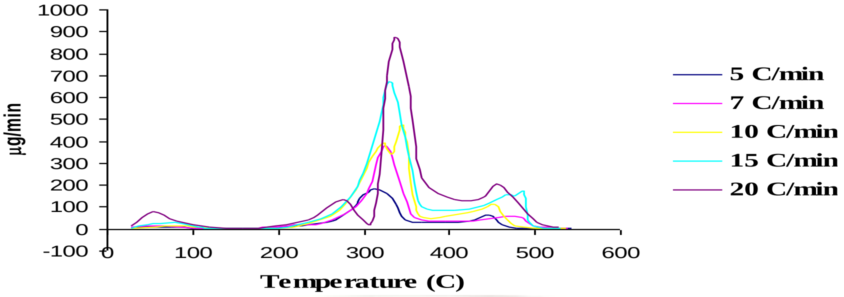


Fig 3 DTG Curves

Table 2 DTG Values for Different Heating Rates

Heating Rate (β)	DTG $_{max}$ (mg/min)	Temperature corresponding DTG $_{max}$ ^{0}C
5	187	311.2
7	380	324.9
10	392	322.2
15	673	331.6
20	876	338.3

Table 3 Values of Kinetic Constants for Different Heating Rates

Heating Rate (^{0}C/min)	First Stage		Second Stage		Third Stage	
	E kJ/mol	A min^{-1}	E kJ/mol	A min^{-1}	E kJ/mol	A min^{-1}
5.0	5.0	100.03	61.94	185.7	104.86	165.12
7.0	7.0	112.41	1.6 x10^{3}	191.11	2.4 x10^{3}	163.08
10.0	10.0	113.93	1.7 x10^{3}	187.58	2.8 x10^{3}	185.32
15.0	15.0	116.29	4.5 x10^{3}	199.8	6.9 x10^{3}	179.63
20.0	20.0	122.27	1.1 x10^{3}	198.9	1.7 x10^{4}	186.11

4.2 Pyrolysis

Fig.4 represents the weight loss of glossy paper with respect to temperature which shows that the first stage is less extended from room temperature to temperature of 271 ^{0}C due heat and mass transfer resistance which resists the heat diffuse in the card board and hence high amount of pyrolytic oil is collected.

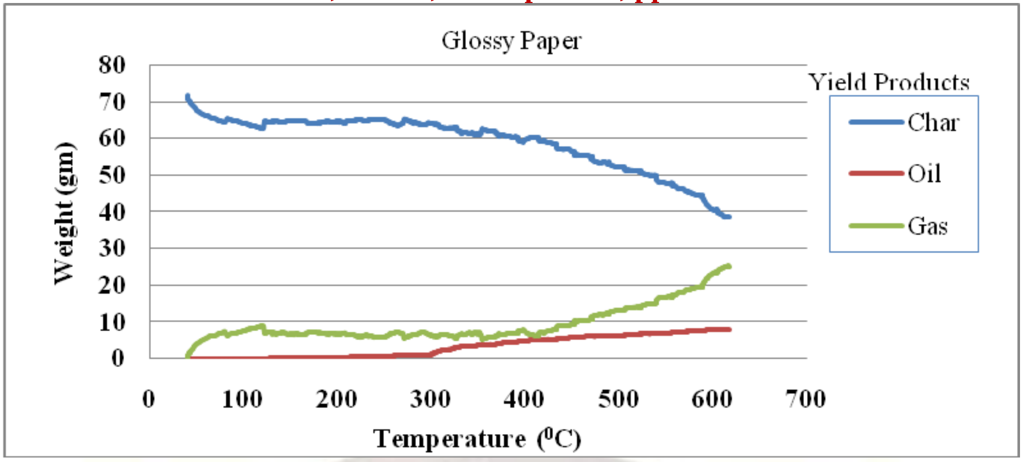


Fig. 4 Weight Variation of Glossy Paper Yield Products with Temperature Rise

Table 4 indicates the elemental analysis of card board yield products which shows that the presence of nitrogen and sulfur is almost absent in yield products which establish the acceptance of yield products as fuel. Table 4 also indicates that the gross calorific values yield products are quite high so card board waste can become good alternative fuel.

Table 4 Ultimate Analysis Yield Product

	Carbon (% wt.)	Hydrogen (%wt.)	Nitrogen (%wt.)	Sulfur (%wt.)	Oxygen (% wt)	GCV kJ/kg
Pyrolytic Oil	44.11	5.92	0.02	Absent	49.35	1507.32
Char	36.82	Absent	Absent	Absent	0.71	8248.39

Table 5 shows the proximate analysis of yield products (char and pyrolytic oil). The moisture content in pyrolytic oil almost is 30 % except in textile waste. The volatile matter is 60% in pyrolytic oil similarly for char the fixed carbon is 37 %. The ash content is low in case of oil but high in case of char may be because of heat mass transfer resistance the lack of decomposition of the card board. This established the potential of both pyrolytic oil and char as an alternative fuel for any thermal system.

Table 5 Proximate Analysis Yield Product

	Moisture (% wt)	Volatile Matter (% wt)	Fixed Carbon (% wt)	Ash (% wt)
Pyrolytic Oil	31.11	63.61	4.68	0.60
Char	0.01	1.20	36.32	62.47

Table 6 shows the gas composition of yield product. Since the synergy gases (CO, CO_2, H_2O, and HC) contained a high calorific value, their use as marketable fuels greatly supports the recycling of the card board waste constituents in MSW.

Table 6 Gas Composition of Product Gas

Butane (%wt.)	Carbon Dioxide (%wt.)	Carbon Monoxide (%wt.)	Oxygen (% wt.)	Ethane (%wt.)	Propane (%wt.)	Methane (%wt.)	Nitrogen (%wt.)
ND	6.44	7.781	2.8	2.76	3.5	35.92	40.799

Table 7 shows the summary of product yield and its GCV which shows that with help of pyrolysis process good quantity of char, pyrolytic oil and product gases are obtained from the card board and may be used as energy source with minimum environment contamination.

Table 7 Yield Products Composition

Yield Products Distribution in % of Sample			GCV kcal/kg		
Char	yrolytic Oil	roduct Gas	Char kcal/kg	Pyrolytic Oil kcal/kg	Product Gas kcal/m^3
53.85	11.25	34.88	1970	360	3000

4.3 Char Charactersation

The char which remain after the decomposition of glossy paper waste at 10^0C/min and 20^0C/min are analyzed with the help of in scanning electron microscope (JEOL 5610LV) with Energy Dispersive Spectroscopy (EDS); which is helpful to select the method for extracting some of the important elements from the char as well as to decide the possible use of char in power plant as a blending mixture. Fig. 5 to 8 show the elemental analysis of char of glossy paper waste

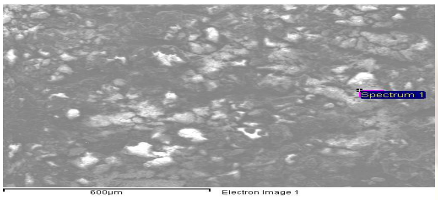


Fig. 5 Glossy paper Residues (10 ^{0}C/min)

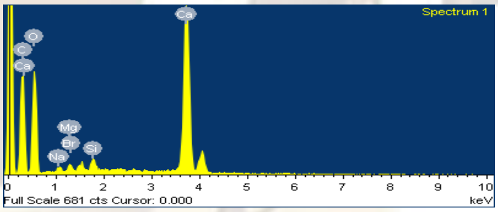


Fig. 6 Elemental Spectrm

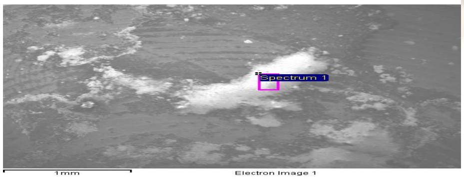


Fig. 7 Glossy paper Residues (20 ^{0}C/min)

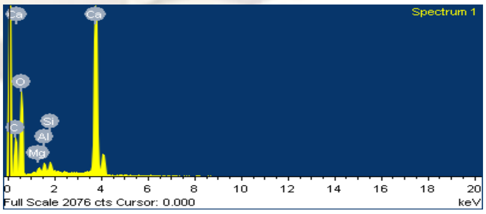
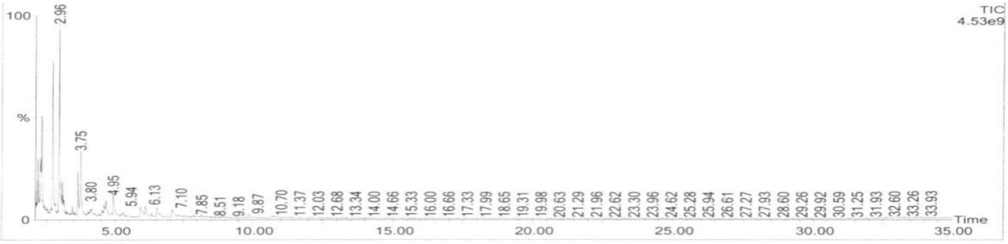


Fig. 8 Elemental Spectrm

4.4 GC- MS

Fig 9 shows the Gas Chromatography-Mass Spectroscopy results of pyrolytic oil which shows the presences of different important chemicals in the pyrolytic oil with their percentages. The Mass spectroscopy Gas chromatography is an analytical technique to evaluate the existence of different chemical compositions present in pyrolytic oil. The methods also important because some chemical compositions which are produced at low temperature also get condensed and their existence can be evaluated by this technique.



#	RT	Area	Area %	Mw	MOL. FORM	COMPOUND NAME
1	2.19	32,256,000	5.054	57.00	C2H3NO	Methane, isocyanato-
2	2.30	30,247,836	4.739	131.0	C5H9NO3	4-Hydroxyproline
3	2.33	64,178,368	10.06	112.0	C8H16	Cyclopentane, 1,2,3-trimethyl-
4	2.73	123,043,576	19.28	54.00	C4H6	1,3-Butadiene
5	2.96	157,574,240	24.69	53.00	C3H3N	2-Propenenitrile
6	3.09	26,184,202	4.103	117.0	C5H11NO2	2-Methylaminomethyl-1,3-dioxolane
7	3.14	10,087,348	1.581			
8	3.64	26,979,760	4.227	68.00	C5H8	1-Butyne, 3-methyl-
9	3.75	54,073,124	8.473	226.0	C8H10N4O4	Sydnone, 3,3'-tetramethylenedi-
10	4.61	9,954,739	1.560	110.0	C6H6O2	2-Furancarboxaldehyde, 5-methyl-
11	4.68	17,092,330	2.678	68.00	C5H8	1-Butyne, 3-methyl-
12	4.95	20,300,144	3.181	94.00	C6H6O	Phenol
13	5.94	20,973,278	3.286	112.0	C5H4O3	2H-Pyran-2,6(3H)-dione
14	6.13	13,150,279	2.060	54.00	C4H6	1,3-Butadiene
15	7.10	14,380,157	2.253	222.0	C10H10N2O2S	5-(4-Hydroxy)-benzyl-2-thioxo-

Fig. 9 Gas Chromatography-Mass Spectroscopy of Glossy Paper

5 Conclusions

The activation energy for rate of 5^0C/min to 20^0C/min varies in the rate of 92.70 kJ/mol to 114.56 kJ/mol in first stage, 173.59 kJ/mol to 192.49 kJ/mol for second stage and 184.40kJ/mol to 187.41 kJ/mol in third stage.The decomposition rate and corresponding peak temperature in the heating rate in the range of 5^0C/min to 20^0C/min is observed to be in the range of 187 to 876 mg/min with peak temperature in the range of 311.2 ^{0}C to 338.3 ^{0}C. The relative yield of char, pyrolytic oil and gas are observed to be 53.85 %, 11.25 % and 34.88 % respectively. The decomposition occurs at a slower rate in case of glossy paper among different paper waste.

References:

1 Joseph, K., Perspectives of solid waste management in India , *Proc International Symposium on the Technology and Management of the treatment and Reuse of the Municipal Solid Waste* ,2002.

2 Sudhir Kumar, Technology options for municipal solid waste-to-energy project**,** *TERI Information Monitor on Environmental Science , 5(1),* 2000

3 Morcos V.H, Energy recovery from municipal solid waste incineration – A review, *Heat Recovery Systems and CHP, 9*, 1989, 115-126.

4 Saxena S.C., Jotski C.K., Fluidized-bed incineration of waste materials' *Progress in Energy and Combustion Science 20* 1994 281-324

5 Akolkar, A.B. 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, *J.Waste Manag.29(2)*, 2009, 883-895

6 Chettiyappan Visvanathan, Mechanical-biological pre-treatment of Municipal Solid Waste in Asia, , *Proc International Symposium MBT*, 2005

7 Garcia A.N., Marcilla A., Font R., Thermogravimetric kinetic study of the pyrolysis of municipal solid waste, *Thermochimica Acta,254* ,1995, 277- 304

8 David C., Salvador S., Dirion J.L. and Quintard M., Determination of a reaction scheme for cardboard thermal degradation using thermal gravimetric analysis**,** *J. Anal. Appl. Pyrolysis* 67, 2003 307- 323

9 Chao-Hsiung Wu, Pyrolysis Kinetics of Paper Mixture in Municipal Solid Waste, *Journal of Chem.Tech. Biotechnol, 66*, 1997, 65-74

10 Sorum L.,.Gronli M.G. and Hustad J.E**,,** Pyrolysis Characteristics and Kinetics of Municipal Solid Waste *Fuel ,80*, 2001, 1217-1227

11 JIN Yu-qi , Study on the comprehensive combustion kinetics of MSW, *Journal of Zhejiang University Science* ,2003

12 Chao- Hasiung Wu, Pyrolysis Product Distribution of Waste Newspaper in MSW, *Journal of Analytical and Applied Pyrolysis, 60*, 2002, 41-53

13 Bhuiyan, On Thermal Stability and Chemical Kinetics of Waste Newspaper by Thermogravimetric and Pyrolysis Analysis, *Journal of Environment and Engineering 3*, 2008, 1-11

14 F. Paradela F. Pinto I. Gulyurtlu I. Cabrita, Clean Techn Environ Policy 11,2009,115–122

15 Kuen-Song Lin, H. Paul Wang, S.-H. Liu, Ni-Bin Chang, Y.-J. Huang, H.C. Wang, *Fuel Processing Technology 60*,1999, 103–110

16 Ch. Pasel, W. Wanzl, Experimental Investigation on Reactor Scale-up and Optimisation of Product Quality in Pyrolysis of Shreader Waste *Fuel Processing Technology 80*; 2003 47– 67

17 S. Ojolo and A. Bamgboye. Thermo chemical Conversion of Municipal Solid Waste to Produce Fuel and Reduce Waste, *Agricultural Engineering International: the CIGR E-Journal 6*, 2005.

18 Yourlmaz S, Investigation of emissions and combustion kinetics of waste wood samples with thermal and spectral methods, PG diss, Middle East Technical University, 2006