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PYROLYSIS AND OXIDATION KINETICS OF MEDICAL WASTES

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ABSTRACT

On account of the infectious properties of medical wastes, most are treated carefully by incineration to ensure proper destruction of pathogens. However, the behaviors of medical wastes are not well understood during the process of incineration. Thus, the aim of this work is to investigate pyrolysis and oxidation kinetics of the medical wastes, including cottons, gauzes, saline bottles, stomach medicines with the thermal gravimetric analysis (TGA) method. Experimentally, the degradation of cottons and saline bottles in pyrolysis and oxidation occurred at about 530 K and 510 K as well as 630 K and 530 K, respectively. Oxygen affects the degradation reaction of cottons and saline bottles at lower temperatures. The rate equations of the first stage of thermal treatment in different oxygen contents also showed that oxygen would decrease the activation energies of decomposition of cottons, gauzes and saline bottles. But the presence of oxygen did not influence the decomposition of stomach medicines at temperatures below 550 K, while only pyrolysis took place.

Keywords: Medical wastes, incineration, pyrolysis, oxidation, kinetics

INTRODUCTION

In Taiwan, about 280 tons of medical wastes are generated daily from hospitals, medical institutions, medical laboratories, medical research organizations, biotechnology institutions, and other organizations during medical treatments, examinations, researches, or productions [1]. The various types of these medical wastes are infectious wastes, pathological wastes, radioactive wastes, biochemical wastes, anatomical wastes, contaminated sharps and waste medicines. They can easily cause harm to humans and the environment if handled improperly [2,3]. Additionally, different types of medical wastes contain their own specific characteristics and therefore require different disposal methods [4]. The EPA report in Taiwan [1] indicated that about 85 percent of medical wastes fell into the category of general wastes and could be disposed of along with other general wastes. The remaining 15 percent of the medical wastes were typically infectious wastes and had to be treated by incineration or with other methods.

Combustible medical wastes contain various kinds of materials, such as cottons, gauzes, medicines, surgical masks, surgical gloves, saline bottles and bags, syringes, and so on. Although a greater portion of the combustible waste could be recovered or recycled, these combustible medical wastes are treated by incineration or sterilization to ensure the proper destruction of pathogens [5]. Incineration has consistently been effective in disinfecting contaminated wastes, destroying hazardous organic compounds and reducing waste volumes [6]. However, these medical waste incinerators are potential sources of various air pollutants. Depending upon the waste type, the incinerator type and the operating condition, certain pollutants such as particulate matter (PM), CO, chlorinated dibenzo dioxins, dibenzo furans (CDD/CDF), HCl, SO_2, NO_x, and metals can be emitted [7].

In order to provide the operational parameters and the design criteria of thermal disposal systems, pyrolysis and oxidation kinetics of medical wastes were studied. Thermogravimetric analysis (TGA) is widely used as a method to investigate the thermal decomposition of the polymers and to determine the kinetic parameters such as activation energy, pre-exponential factor, and the reaction order [8-22]. The fact that the data of TGA could be transferred to a reaction kinetic parameter is based on the classical laws of kinetics [15,16].

Thus, the objective of the present study is to determine the pyrolysis and oxidation kinetics of various kinds of medical wastes. The corresponding activation energy, pre-exponential factors and the order of reactions are also examined.

MATERIALS AND METHODS

The medical wastes (cottons, gauzes, saline bottles and stomach medicines (Nacid Tablet)) were provided by a local hospital in Tainan. The elemental compositions of these medical wastes were measured by Elemental Analyzer (elementar vario EL III) and are shown in Table 1.

The pyrolysis and oxidation kinetics studies of the medical wastes were investigated by using a thermogravimetric analyzer (TGA) (SDT 2960, TA Instruments). About 10 mg of the medical wastes were heated in a flowing gas (0, 5.3, 10.5, 21% O_2)/N_2 (100 ml min^{-1}) at different heating rates of 2, 5, and 8 K min^{-1} at 300-1173 K in the TGA experiments. The weight of the medical wastes were recorded at 10-second intervals. The calibration procedures for the TGA/DTA (differential thermal analysis) baseline and temperature were performed once a month. In all experiments, aluminum oxide was used as a temperature reference.

RESULTS AND DISCUSSION

Pyrolysis and Oxidation Reaction

Medical cottons are usually used in cleaning or disinfecting the wounds on patients. They can be found in any emergency room, surgical operation room or sickroom. Because they have direct contact with the patient's skin and body fluid, these infectious waste cottons must be treated by incineration. Figure 1(a) shows the thermal gravimetric analysis of pyrolysis and oxidation of the cottons. The main degradation reaction of the cottons in pyrolysis and oxidation occurred at about 530 K and 510 K, respectively. The derivative thermal gravimetric (DTG) curve shows that the maximun weight loss by pyrolysis and oxidation occurred at 591 K and 556 K, respectively and the reaction stages were different in both pyrolysis (one stage) and oxidation (three stages). In the first stage, hydrocarbons were decomposed at lower temperatures in the exothermic oxidation process. However, the remaining percentages of cottons after pyrolysis and oxidation were 23% and 11%. It seems that oxygen would enhance the degradation reaction of the cottons. If there is not enough oxygen at the temperature above 630 K in the incinerator, the cottons would not be completely decomposed.

Medical gauzes are used to protect and stabilize patients' wounds and also to prevent those wounds from infection. Waste gauzes are generated mostly from nursing stations, sickrooms, surgical operation rooms, treating places, isolation wards, delivery rooms and so on. Figure 1(b) shows the typical TGA curves in the pyrolysis and oxidation of the gauzes. The main degradation reaction of the gauzes in pyrolysis and oxidation occurred at about 550 K. The derivative thermal gravimetric (DTG) curve also shows that the maximun weight loss in pyrolysis and oxidation occurred at 617 K and 586 K, respectively. It seems that in the first stage (550-650 K), the TGA curves of the pyrolysis and oxidation of the gauzes were very similar. The presence of oxygen did not obviously influence the primary decomposition of the gauzes. However, the gauzes were decomposed in the presence of oxygen at temperatures higher than 650 K and the remains would be oxidized from 18% (in nitrogen) to 7% (in air).

Saline is provided to patients for the purpose of supplying their blood with water and electrolytes, and for diluting toxins. Waste saline bottles generally come from nursing stations, sickrooms, surgical operation rooms, treating places, isolation wards, blood dialysis rooms and delivery rooms. Since these bottles contain quite large quantities of carbon (84.54%) and chloride (7.66%), such characteristics would make thermal treatments complicated. A typical TGA curve obtained from the pyrolysis and oxidation of the saline bottles is shown in Figure 1(c). The degradation of the saline bottles in pyrolysis and oxidation occurred at about 630 K and 530 K, respectively. This specifically showed that oxygen affected the degradation reaction of the saline bottles in the temperature range 530-630 K. Some organic contents could be decomposed more easily in oxidation than in pyrolysis. However, either in the pyrolysis or in the oxidation of the saline bottles, the combustible contents could be decomposed completely at 760 K. The ash was less than 9%.

Stomach medicines (Nacid Tablet) are usually found in hospitals, drug stores or homes. When people throw these waste medicines away arbitrarily, they can cause serious pollution. The thermal gravimetric analysis of the stomach medicine by pyrolysis and oxidation is shown in Figure 1(d). The pyrolysis and oxidation reaction of the stomach

Table 1. Elemental composition of the medical wastes.

Medical Wastes	**Carbon (%)**	Hydrogen (%)	Oxygen (%)	**Nitrogen (%)**
Cottons	42.10	6.41	49.12	1.25
Gauzes	41.81	6.33	43.60	1.36
Saline bottles	83.54	2.98	3.13	2.65
Stomach medicines	20.81	5.19	4.57	0.69

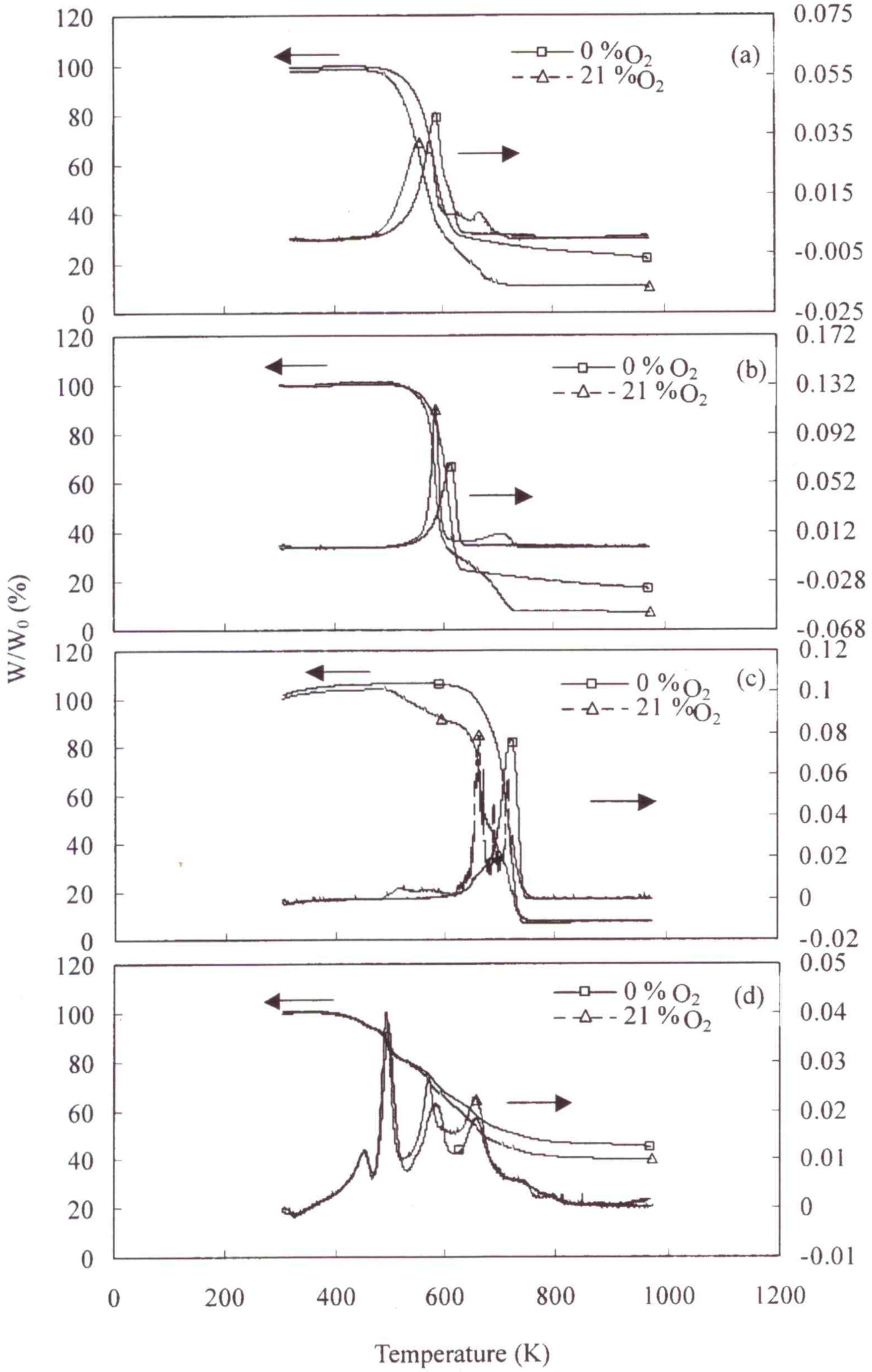

Figure 1. The thermal gravimetric analysis by pyrolysis and oxidation of the (a) cottons, (b) gauzes (c) saline bottles and (d) stomach medicines.

medicines were complex. There were four reaction stages of pyrolysis and oxidation for stomach medicine by the TGA in this study. The maximum weight loss of the four stages by pyrolysis and oxidation occurred at 456, 493, 578 and 658 K. But in the first and second stages, the lines corresponding to each run could not be distinguished since they lay together. It seems that the presence of oxygen did not influence the decomposition of the stomach medicines at temperatures less than 550 K, while only pyrolysis took place. At temperatures above 550 K, oxygen would enhance the degradation reaction and the remaining portions of the stomach medicines after pyrolysis and oxidation were about 46% and 37%.

Kinetics Reaction

The kinetic parameters (such as the activation energy, reaction order and pre-exponential factor) for the oxidation of the resin were numerically calculated from the TGA weight loss data (with heating rates of 4, 5 or 8 K min^{-1}) by using the modified Friedman algorithm [22-24]. The overall rate equation of conversion factor is expressed in the Arrhenius relation forms,

$$\frac{dx}{dt} = A\ \exp(-Ea/RT)\ (1-x)^n\ [O_2]^m \tag{i}$$

$$x = \frac{w_o - w}{w_o - w_f} \tag{ii}$$

$$k = A\ \exp(-Ea/RT) \tag{iii}$$

where t is the time (sec); A is the pre-exponential factor (sec^{-1}); Ea is the activation energy (cal mol^{-1}); T is the reaction temperature (K); R is the universal gas constant (1.987 cal mol^{-1} K^{-1}); w is the mass of the sample at time t, and w_o and w_f are the initial and final (or residual) mass of the medical wastes, respectively. The x represents conversion, with the n and m as the reaction orders for the unreacted medical wastes and oxygen, respectively, and k as the rate constant (sec^{-1}).

The rate equations of the first stage for cottons, gauzes, saline bottles and stomach medicines under thermal treatments in different oxygen content are shown in Table 2. However, the TGA curve showed that oxygen did not influence the decomposition of the stomach medicines at the first stage. Therefore only the rate equation of pyrolysis of stomach medicines is shown in Table 2. The numerical calculation from TGA weight loss data at different heating rates showed that in the first stage, the activation energies for pyrolysis and oxidation of the cottons were 40-43 and 20-30 kcal mol^{-1}, the gauzes were 43-46 and 32-38 kcal mol^{-1}, the saline bottles were 62-83 and 55-70 kcal mol^{-1} and the stomach medicines 23-31 kcal mol^{-1}, respectively. Oxygen decreased the activation energies of decomposition of cottons, gauzes and saline bottles. The rate equation of the first stage for cottons, gauzes and saline bottles under thermal treatments in air also showed that $dx/dt = 6.09\times10^{12} \exp(-20497/RT)\ (1-x)^{0.28}\ [O_2]^{4.17}$, $dx/dt = 8.48\times10^{13} \exp(-32456/RT)\ (1-x)^{0.24}\ [O_2]^{1.83}$ and $dx/dt = 2.79\times10^{7} \exp(-60318/RT)\ (1-x)^{0.72}\ [O_2]^{3.69}$, respectively. The rate limiting step might be the diffusion of oxygen through the surface of these wastes.

In the future, an incinerator for destruction of medical wastes at lower temperatures around 550 K should be maintained in controlled air to advance decomposition for some medical wastes, and at higher temperatures > 850 K enough oxygen should be provided to ensure pathogen kill, sterile ash and less ash quantity.

Table 2. The rate equations of the first stage for medical wastes under thermal treatments in different oxygen contents.

Medical wastes	$O_2/(O_2+N_2)$ (%)	The rate equations
Cottons	0	$dx/dt=3.61\times10^{14}\exp(-42143/RT)(1-x)^{0..62}$
	5.3	$dx/dt=6.09\times10^{12}\exp(-33829/RT)(1-x)^{0.5}[O_2]^{4.17}$
	10.5	$dx/dt=6.09\times10^{12}\exp(-30123/RT)(1-x)^{0.32}[O_2]^{4.17}$
	21	$dx/dt=6.09\times10^{12}\exp(-20497/RT)(1-x)^{0.28}[O_2]^{4.17}$
Gauzes	0	$dx/dt=4.47\times10^{14}\exp(-44219/RT)(1-x)^{0.49}$
	5.3	$dx/dt=8.48\times10^{13}\exp(-37474/RT)(1-x)^{0.41}[O_2]^{1.83}$
	10.5	$dx/dt=8.48\times10^{13}\exp(-34628/RT)(1-x)^{0.39}[O_2]^{1.83}$
	21	$dx/dt=8.48\times10^{13}\exp(-32456/RT)(1-x)^{0.24}[O_2]^{1.83}$
Saline bottles	0	$dx/dt=8.88\times10^{20}\exp(-71112/RT)(1-x)^{0.86}$
	5.3	$dx/dt=2.79\times10^{7}\exp(-66019/RT)(1-x)^{0.94}[O_2]^{3.69}$
	10.5	$dx/dt=2.79\times10^{7}\exp(-62959/RT)(1-x)^{0.79}[O_2]^{3.69}$
	21	$dx/dt=2.79\times10^{7}\exp(-60318/RT)(1-x)^{0.72}[O_2]^{3.69}$
Stomach medicines	0	$dx/dt=5.12\times10^{5}\exp(-36532/RT)(1-x)^{1.66}$

CONCLUSIONS

By TGA, the degradation of cottons and saline bottles by pyrolysis and oxidation occurred at about 530 K and 510 K as well as 630 K and 530 K, respectively. It specifically showed that oxygen affected the degradation reaction of cottons and saline bottles at lower temperatures. Some organic contents could be decomposed more easily in oxidation than in pyrolysis.

The rate equations of the first stage of the thermal treatment in different oxygen contents also showed that oxygen decreased the activation energies of decomposition of cottons, gauzes and saline bottles from 40-43, 43-46, 62-83 kcal mol^{-1} (pyrolysis) to 20-30, 32-38, 55-70 kcal mol^{-1} (oxidation), respectively. But the presence of oxygen did not influence the decomposition of stomach medicines at temperatures < 550 K, while only pyrolysis took place.

The remaining percentages of the cottons, gauzes and stomach medicine after pyrolysis and oxidation were from 23%, 18%, 46% (in nitrogen) to11%, 7%, 37% (in air), respectively. It seems that an incinerator for destruction of medical wastes at higher temperatures > 850 K should be provided with enough oxygen to ensure the combustible contents could be decomposed completely.

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REFERENCES

1. Taiwan EPA, EPA urges local governments to properly treat medical waste. *Environ. Policy Monthly*, **4**, 5-6 (2001).
2. Birchard K., Out of sight, out of mind ... the medical waste problem. *The Lancet*, **359**, 56 (2002).
3. Almuneef M. and Memish Z., A.Effective medical waste management: it can be done. *Am. J. Infect. Control*, **31**, 188-192 (2003).
4. Lee, C. C. and Huffman G. L., Medical waste management/incineration. *J. Hazard. Mater.*, **48**, 1-30 (1996).
5. Jangsawang W., Fungtammasan B. and Kerdsuwan S., Effects of operating parameters on the combustion of medical waste in a controlled air incinerator. *Energ. Convers. Manage.*, **46**, 3137-3149 (2005).
6. Altin S., Altin A., Elevli B. and Cerit O., Determination of hospital waste composition and disposal methods: a case study. *Pol. J. Environ. Stud.*, **12**, 251-255 (2003).
7. Levendis Y. A., Atal A., Carlson J. B. and Del Mar Esperanza Quintana M., PAH and soot emissions from burning components of medical waste: examination/surgical gloves and cotton pads. *Chemosphere*, **42**, 775-783 (2001).
8. Huang Y. J., Wang H. P. Liu S. H. and Hsiao M. C., Pyrolysis kinetics of spent low-level radioactive resin. *Nuclear Technol.*, **138**, 206-210 (2002).
9. Chen K. S., Yeh R. Z. and Wu C. H., Kinetics of thermal decomposition of epoxy resin in nitrogen-oxygen atmosphere. *J. Environ. Eng-ASCE*, **123**, 1041-1046 (1997).
10. Wu C. H., Chang C. Y., Hwang J. Y., Shih S. M., Chen L. W., Chang F. W. and Yang W. F., Pyrolysis kinetics of tissue paper of MSW. *J. Chinese Inst. Eng.*, **17**, 659-669 (1994).
11. Avni E. and Coughlin R. W., Kinetic analysis of lignin pyrolysis using nonisothermal TGA data. *Thermochim. Acta.*, **90**, 157-167 (1985).
12. Anderson D. A. and Freeman E. S., The kinetics of the thermal degradation of polystyrene and polyethylene. *J. Polym. Sci.*, **54**, 253-260 (1961).
13. Chang C. Y., Wu C. H. and Hor J. L., Pyrolysis kinetics of polystyrene. *J. Chinese Inst. Environ. Eng.*, **2**, 125-133 (1992).
14. Peev G., Trifonova M., Peeva L. and Michallov P., Kinetics of styrene removal from polystyrene by thermal treatment in air. *J. Appl. Polym. Sci.*, **33**, 283-288 (1987).
15. Friedman H. L., Kinetics of thermal degradation of char-forming plastics from thermogravimetry, application to a phenolic plastic. *J. Polym. Sci. Part C.*, **6**, 183-195 (1965).
16. Petrovis Z. S. and Zavargo Z. Z., Reliability of methods for determination of kinetic parameters from thermogravimetry and DSC measurements. *J. Polym. Sci.*, **32**, 4353-4367 (1986).
17. Nishizaki H., Yoshida K. and Wang J. H., Comparative study of various methods for thermogravimetric analysis of polystyene degradation .*J. Appl. Polym. Sci.*, **25**, 2869-2877 (1980).
18. De La Puente G., Marbán G., Fuente E. and Pis J. J., Modelling of volatile product evolution in coal pyrolysis. the role of aerial oxidation. *J. Anal. Appl. Pyrolysis*, **44**, 205-218 (1998).
19. Ibáñez R., Andrés A., Viguri J. R., Ortiz, I. and Irabien, J. A., Characterisation and management of incinerator wastes. *J. Hazard. Mater.* **79**, 215-227 (2000).
20. Gómez-Rico M. F., Martín-Gullón I., Fullana A., Fullana A., Conesa J. A. and Font R., pyrolysis and combustion kinetics and emissions of waste lube oils. *J. Anal. Appl. Pyrolysis*, **68-69**, 527-546 (2003).

21. Popescu C., Segal E. and Iditoiu C., A kinetic model for the thermal decomposition of wool. *Thermochim. Acta*, **256**, 419-427 (1995).
22. Chen Y. and Mori S., Estimating the combustibility of various coals by TG-DTA. *Ener. Fuels.*, **9**, 71-74 (1995).
23. Reich L. and Levi D. W., Dynamic thermogravimetric analysis in polymer degradation. *Macromol. Rev.*, **1**, 173-275 (1967).
24. McNeill I. C., Ackerman L. and Gupta S. N., Degradation of polymer mixtures. IX. Blends of polystyrene with polybutadiene. *J. Polym. Sci.: Polym. Chem. Edit.*, **16**, 2169-2181 (1978).