

PYROLYSIS PRODUCT DISTRIBUTION OF WASTE TOILET PAPER IN A LABORATORY-SCALE TGA REACTOR

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Key Words : Toilet paper, pyrolysis products, thermogravimetric analysis

ABSTRACT

Waste toilet paper is one of the principal components in municipal solid waste (MSW) in Taiwan. Since toilet paper contained a high calorific value, its conversion by the pyrolysis method to marketable fuels has become a noble goal from not only an economic, but also from an environmental standpoint. In this study, the waste toilet paper was pyrolyzed with a laboratory-scale thermogravimetric analysis (TGA) reaction system. The pyrolysis experiments were carried out in nitrogen environment at a constant heating rate of 5 K min^{-1} . The pyrolysis products and the residues were collected and analyzed by gas chromatography and elemental analysis, respectively. The major products investigated included non-hydrocarbons (H_2 , CO , CO_2 and H_2O) and hydrocarbons (C_{1-3} , C_4 , C_5 , C_6 , 1-ring, C_{10-12} , levoglucosan, C_{13-15} and C_{16-18}). The cumulated masses and the instantaneous concentrations of pyrolysis products were obtained under the experimental conditions. The yields of the major products were 0.35% for H_2 , 12.82% for CO , 47.31% for CO_2 , 28.29% for H_2O , and 2.55% for HCs, respectively. Levoglucosan was the major compound of hydrocarbons. The estimation of the mass of tar, yielded at various pyrolysis temperatures, was also made. The results of this study might be useful for the design of pyrolysis process as well as for understanding the pyrolysis mechanisms of the toilet paper.

INTRODUCTION

The disposal of municipal solid waste has become an increasingly intricate and costly problem because of the decrease in the available space for landfills and the growing concern about the living environment. Some studies and reviewed literature have indicated that a proper thermal pyrolysis method might be useful for resolving the disposal problems

and making an energy conversion from MSW [1-5]. Typically, on a dry basis, MSW consisted of paper (28.95%), cellulosic cloth (8.11%), yard waste (3.10%), food (23.18%), plastic (19.59%), leather and rubber (0.43%), metals (7.89%), glass (6.98%), and ceramic, earthen materials and miscellaneous (1.77%) in Taiwan [6]. The mass percentages of the waste tetra pack, printing and writing papers (newspaper and coated/uncoated paper), and other papers (toilet paper,

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wrapping paper, etc.) in MSW were about 20.75, 22.8 and 56.48 %, respectively [7]. The annual yields of the toilet paper (tissue and sanitary paper) were about 69,243 - 112,596 tons (or 15-16 % of the domestic market) through 1982 - 1988 [8]. Since the toilet paper waste contained a high calorific value of about 17,200 kJ kg⁻¹ dry weight, its conversion to marketable fuels has become a noble goal from not only an economic, but also from an environmental standpoint.

Toilet paper is one of the cellulosic materials. It consists mostly of chemical pulp and a fraction of mechanical pulp. Cellulose and hemicellulose are the principal components of chemical and mechanical pulps, respectively. Studies on the pyrolysis of cellulose and hemicellulose have been performed by many researchers. These studies were concerned mostly about the thermal degradation of pure cellulose or hemicellulose and focused on the analyses of products [9-11], the effects of reaction conditions [12], the reaction mechanisms and the pyrolysis kinetics [13-16]. Some studies have been conducted to investigate the pyrolysis kinetics [17-22] and products [23-26] of waste papers. Cozzani *et al.* [17] have investigated the pyrolysis behavior of different refuse derived fuels (RDFs) at the typical heating rates of conventional pyrolysis process. The main RDF components were paper, wood-like materials, and plastics mainly polyethylene (PE). A kinetic model has been established to describe the thermal degradation of RDFs. Also, a simplified two-reaction model has been proposed to illustrate the pyrolysis kinetic behavior of tissue paper [18], uncoated [19]/coated [20] printing and writing papers and paper mixtures [21] over 450 - 850 K temperature range. The corresponding activation energies, pre-exponential factors and reaction orders for four type waste papers (newspaper, uncoated/coated printing and writing paper and tissue paper) have been determined in the experimental conditions. Sorum *et al.* [22] have explored the pyrolysis characteristic and kinetics of MSW. The results have shown (indicated) that the cellulosic fraction of MSW is modeled by three independent parallel reactions describing the degradation of hemicellulose, cellulose, and lignin. The reactivity of cellulosic matter is increased in a mixture with polyvinyl chloride (PVC). Galletti *et al.* [23] have investigated the pyrolysis products of paperboards from waste paper and wheat straw pulps. The results have indicated that the pyrolytic compounds from straw pulp and from waste paper pulp are essentially the same. Li *et al.* [24] have investigated the pyrolysis products of MSW components (paper, paperboards, PVC, PE, rubber, vegetal materials, wood and orange husk) by a laboratory-scale rotary kiln. The effects of heating methods, moisture contents and size of waste on the pyrolysis gas and compositions have been evaluated. Wu *et al.* [25] have investigated the pyrolysis products of uncoated printing and writing paper of MSW. The cumulated masses

and the instantaneous concentrations of gaseous products have been determined under experimental conditions. Wu *et al.* [26] have explored the pyrolysis product distribution of waste newspaper in MSW. The results indicated that the yields of non-hydrocarbons and of hydrocarbons at 938 K were about 88.45 and 2.11%, respectively. The results of previous studies have provided us with some knowledge of determining the pyrolysis kinetics and products of cellulose, hemicellulose, and some cellulosic materials but they have not provided the related data about the pyrolysis products distribution of toilet paper of MSW.

Thus the aim of the present work was to deal with toilet paper of MSW with a view of providing the major products distribution as well as the variations of cumulated masses of pyrolysis products, residues and estimated tar with pyrolysis temperature. The pyrolysis of toilet paper was studied by the thermal gravimetric analysis (TGA) reaction system at a constant heating rate of 5 K min⁻¹. The experiments were carried out over a wide temperature range (450 - 950 K) and in the absence of gasifying agents. Nitrogen was used as the carrier gas. The pyrolysis products and the residues were collected and analyzed by gas chromatography (GC) and elemental analyzer. All these results were useful for determining the pyrolysis mechanisms and for applying the pyrolytic treatment of the waste toilet paper of MSW.

EXPERIMENTAL

Materials

Commercial-grade toilet paper was used in this study. It was purchased from the Kimberly-Clark Co., Ltd. (Taiwan), with the properties described previously [18]. The nitrogen was purchased from the Ching Feng Harnng Co., Ltd. of Taiwan, purity 99.9999%.

Pyrolysis Apparatus and Procedures

The experiments of the pyrolysis of toilet paper were carried out with a TGA reaction system reported in our previous paper [26]. The electrical balance (Cahn-1000, USA; with 0.001 mg readability) was used. A sample of known mass (20 ± 0.5 mg) was placed on a small quartz disk (with 2 cm diameter and 1 mm thickness). The disk was hung on the suspension wire (made of platinum with 0.18 mm diameter) of the balance and enclosed in a quartz shell and tube reactor. The outer shell was 27 cm long with a 3.8 cm inside diameter. The inner tube was 22 cm long with a 1.2 cm inside diameter. The nitrogen at a high flow rate was first introduced into the rear channel of the balance protector for 1 h to purge out the residual oxygen. It was then adjusted to the desired flow rate

($50 \text{ cm}^3 \text{ min}^{-1}$ at 300 K and 1 atm, controlled by a Cole-Parmer N062-01ST rotameter) and switched over to the inner tube of the reactor. After about 0.5 h, the reactor was placed in the furnace (HAS 100/250G with 1,280 W), which had been pre-set to a specified heating rate (5 K min^{-1}). When the control units (Eurotherm 815S with RS232 interface) were all ready, the experimental run of pyrolysis began. At the same time, the variations of the sample mass and of the reaction temperature (probed with a K-type thermocouple) during the entire pyrolysis process were recorded at time intervals of 10 s by the data-processing unit (IBM PC-AT 586 with RS232 interface). The pyrolysis process was operated under atmospheric pressure. The pyrolysis products and the residues were collected at certain specified temperature ranges (or temperatures). The pyrolysis products and the residues were analyzed by a GC and by an elemental analyzer, respectively.

Sampling and Analysis of Volatiles

The volatiles (gas phase at the pyrolysis temperatures) were collected at the exit of a reactor. The discrete sampling and the cumulated sampling methods were employed to collect the volatiles. For the discrete sampling method, the volatiles were collected in the 1 dm^3 sampling bags for the temperatures of 475–950 K in 25 K increments. The temperature of the volatiles before the GC/flame ionization detector (FID), mass spectrometer detector (MSD) analysis was kept at 333 K by an oven. The instantaneous concentrations of volatiles at the temperatures of 488–938 K in 25 K increments corresponded to the temperature ranges described above, respectively. For the cumulated sampling method, the cumulated volatiles corresponding to the principal reaction temperature range (475–950 K) were collected into a 5 dm^3 sampling bag.

The Varian chromatography (equipped with an INCOS 50 B MSD and a Supelco SPB-1 capillary column) was used to identify some major components in the gaseous products. For the analysis of hydrocarbon gases, a China Chromatography 8900 GC (Taiwan) equipped with a FID and a Supelco fused silica capillary column (30 m, 0.53 mm inside diameter, 1.5 μm film thickness) was used. An integrator from Hewlett-Packard (HP 3395) was connected to the GC for graphing and integrating purposes. The conditions for analyzing hydrocarbon gases were set as follows: injector temperature 473 K, detector temperature 523 K, column temperature (following the sampling injection) being held at 308 K for 3 min, nitrogen carrier gas flow rate $10 \text{ cm}^3 \text{ min}^{-1}$, nitrogen makeup gas $30 \text{ cm}^3 \text{ min}^{-1}$, sample volume 0.5 cm^3 . For the analysis of non-hydrocarbon gases (H_2 , CO and CO_2), a China Chromatography 8900 GC equipped with a thermal conductivity detector (TCD) and a Supelco packing

column (60/80 carbonxen-1000, 4.57 m, 2.1 mm inside diameter) was used. An integrator from Hewlett-Packard (HP 3396) was connected to the GC for graphing and integrating purposes. The conditions for analyzing H_2 , CO and CO_2 were set as follows: injector temperature 393 K, detector temperature 333 K, column temperature (following the sampling injection) being held at 308 K for 8 min, helium carrier gas flow rate $25 \text{ cm}^3 \text{ min}^{-1}$ for A and B columns, sample volume 2 cm^3 . The purity of gas standards was 99.9999 % for N_2 , 99.9 % for CO_2 , 99.7% for CO and 99% for H_2 and 100 ppm for $\text{C}_1\text{-C}_6$ in N_2 , respectively. The concentration of H_2O in the gaseous products stream was detected with a psychrometer (HT-3003, Lutron).

Sampling and Analysis of Residues

The mass of used sample for the experiments of sampling and analysis of residues was $20 \pm 0.5 \text{ mg}$. The pyrolytic reactions were stopped at specific temperatures, e. g. 623 and 700 K, so as to collect the residues. The residues corresponding to the pyrolysis temperatures were then analyzed.

The elemental analyses for the initial sample and the residues were made on a Perkin-Elmer, Norwalk, CT 2400 (with 0.3% accuracy) elemental analyzer. The heavy metals in the initial sample were analyzed by the inductively coupled plasma-atomic emission spectrometer (ICP-AES; Germany Kontron S-35). The mass of an initial sample used for the analysis of heavy metals was 100 mg. The sample mixed with strong acids ($3 \text{ cm}^3 \text{ HNO}_3$, $1 \text{ cm}^3 \text{ HClO}_4$, and $1 \text{ cm}^3 \text{ HF}$) was digested at 443 K for 4 h. It was then diluted to 100 cm^3 with pure H_2O and analyzed by the ICP-AES.

RESULTS AND DISCUSSION

Solid Residues

Solid residues, to certain specific extent of mass change, were collected and analyzed by the elemental analyzer for determining the major elements and providing the evidence to support the pyrolysis mechanisms of the two-reaction model [18]. The results of elemental analyses are summarized in Table 1. These results indicated that carbon (C), hydrogen (H) and oxygen (O) were the major constituents of solid residues. The C/H mass ratios of solid residues were about 6.83, 8.61 and 19.59 at pyrolysis temperatures of 300, 623 and 700 K, respectively. The C/O mass ratios of solid residues were approximately 0.93, 1.38, and 2.1 at pyrolysis temperatures of 300, 623 and 700 K, respectively. This indicated that the devolatilization reaction (first stage mass change) was significant from 500 to 660 K [18]. The products of this reaction stage were intermediates and low molecular mass

Table 1. Elemental analyses of initial sample and residues for toilet paper pyrolysis at various temperatures.

Element (%)	300 (K)		623 (K)		700 (K)	
	a	b	a	b	a	b
C	43.07	43.07	52.87	32.79	65.43	8.89
H	6.31	6.31	6.14	3.81	3.34	0.45
O	46.48	46.48	38.29	23.75	31.1	4.23
N	3.3	3.3	2.95	2.35	n.d.*	n.d.
S	n.d.	n.d.	n.d.	n.d.	n.a.#	n.a.
Cl	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.
total (%)	99.16	99.16	100.25	63.37	99.87	13.57
C/H	6.83	6.83	8.61	8.61	19.59	19.76
C/O	0.93	0.93	1.38	1.38	2.1	2.1

^a Based on the mass of residues (dry basis); b: based on the mass of initial sample (dry basis).

* Not detected.

Not analyzed.

Table 2. Principal metals in initial samples (dry basis).

Species	Si	Ca	Al	Mg	Fe	Cr	Mn	Zn	Cd	Pb	total
Conc. (ppmm)	178	1040	31	1140	148	<10	30	<10	<10	<10	2567

volatiles (e. g. H₂, HCs, H₂O, etc.). This was also supported by the product distribution. The sulfur and chlorine in the initial sample and residues were not detected in the elemental analysis (Table 1). This indicated that the potential for treating the pollutants SO_x and HCl from the pyrolysis of waste toilet paper could be negligible. In the second stage of mass change (660 to 950 K), the intermediates further reacted to form volatiles and solid residues. Final residual mass was about 0.5% of the initial sample. The moisture, ash and combustible in the proximate analysis of the initial sample were about 0.58, 0.26 and 99.16%, respectively. Since the ash content was analyzed at 1,073 K in the air environment, we came to realize that the final residual mass percent was higher than that of the ash in the proximate analysis. The major heavy metals in the sample are listed in Table 2. Moreover, because the concentrations of the principal heavy metals (Cr, Cd, Pb) in the samples were less than 10 ppmm, the potential of treating the heavy metals from the pyrolysis of waste toilet paper might be negligible.

Volatiles

Qualitative and quantitative analyses were performed to determine the volatiles (gas phase at the pyrolysis temperatures) in the toilet paper. Qualitative analysis of hydrocarbons was carried out by GC/MSD. The qualitative constituents of hydrocarbons were classified into nine groups according to their retention times. They were methane, ethylene, ethane, propylene and propane (group 1), butene, butane and methanol (group 2), ethanol, furan, pentene and pentane (group 3), hexene, hexane, benzene, butanol, furfural and isoamyl alcohol (group 4), toluene, n-heptane, 1-octene, octane, xylene, styrene, 1-decene, phenol, n-

nonane and dodecene (group 5), naphthalene, dodecane, acenaphthylene and acenaphthene (group 6), levoglucosan (group 7), fluorene, phenanthrene and anthracene (group 8) and fluouanthene, pyrene, benzo(a)-anthracene and chrysene (group 9). The results indicated that there were some compounds observed in the retention time ranges of polycyclic aromatic hydrocarbons (PAHs, such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluouanthene, pyrene, benzo(a)-anthracene, and chrysene). This suggests that PAHs may be released during the pyrolysis or the incomplete combustion process for treating waste toilet papers. The similar results were also observed by M.B. Hajaligol *et al.* [11] and by Galletti *et al.* [23].

Quantitative analysis of volatiles was analyzed with GC/FID (for HCs), GC/TCD (for H₂, CO, CO₂), and psychrometer (for H₂O). The concentrations of volatiles were calculated using the linear calibration response equations of standards. The equation was generated for each of the gas and liquid standards using a minimum of five different concentrations with three replicates for each concentration. All correlation coefficients (r^2) of linear calibration response curves were great than 0.997. The typical calibration curve of CO₂, for example, with $r^2 = 0.999$ is shown in Fig. 1. The instrumental detection limits (IDL) were 31 ppm for H₂, 67 ppm for CO, 0.13 $\mu\text{g L}^{-1}$ for levoglucosan, and 0.02-0.04 $\mu\text{g L}^{-1}$ for the other hydrocarbons. Since the volatiles contained many hydrocarbon species, hydrocarbons were not quantified one by one except for levoglucosan and C₁–C₅ alkanes. The concentration of each group (except levoglucosan and C₁–C₅ alkanes) was determined by calculating the area-concentration ratios of the volatiles corresponding to the appropriate retention time ranges. The in-

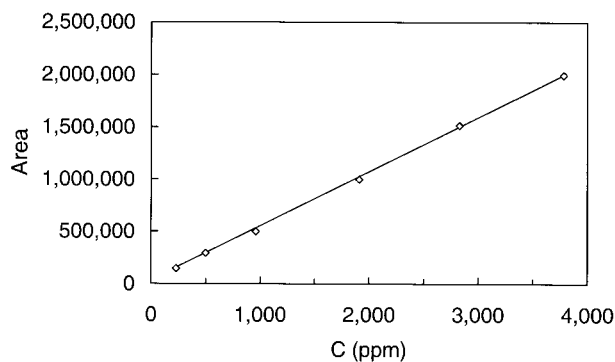
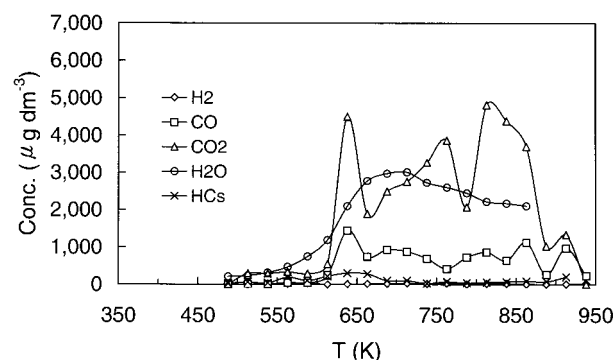
Fig. 1. Calibration curve of CO₂. r₂ = 0.999.

Fig. 2. Variations of instantaneous concentrations of major pyrolysis products at reaction temperature (T).

stantaneous concentrations of volatiles corresponding to the reaction temperatures are shown in Figs. 2-4. The results indicated that the amount of volatiles was negligible for temperatures lower than 488 K. The maximum instantaneous concentrations occurred at about 713 K for H₂, 638 K for CO, 813 K for CO₂, 713 K for H₂O and 638 K for HCs, respectively. On examining the TGA curves [18, 21], we observed two principal reactions as distinguished by the two significant and distinct mass changes over the temperature range of 450–950 K. In the preceding section, it was noted that the release of low molecular mass compounds (H₂, HCs, H₂O, etc.) was significant from 500 to 660 K, while that of volatiles (CO, CO₂, HCs, etc.) by gasification reaction or further pyrolysis of intermediates was significant from 660 to 950 K. Thus, it was supported by the analysis of instantaneous concentrations at various ranges of the reaction temperature.

The analyses of cumulated masses are listed in Table 3 and shown in Figs. 5 and 6. At the pyrolysis temperature of 938 K, the masses of major products relative to the initial sample were 0.35% for H₂, 12.82% for CO, 47.31% for CO₂, 28.29% for H₂O, and 2.55% for HCs, respectively. The percentages of major hydrocarbons relative to the total HCs gases were about 15.69% for group 1 (C₁₋₃), 12.94% for group 3 (C₅), 14.9% for group 4 (C₆), and 36.08% for

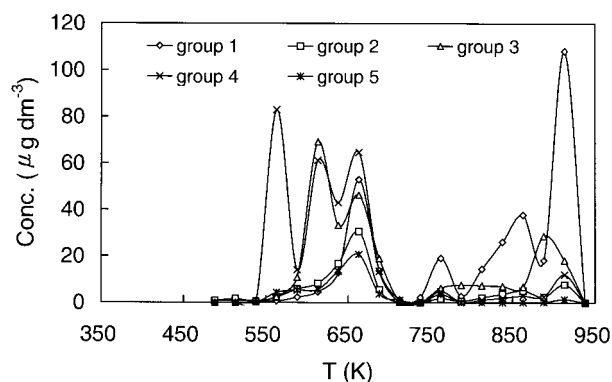


Fig. 3. Variations of instantaneous concentrations of hydrocarbons (groups 1 - 5) at reaction temperature (T).

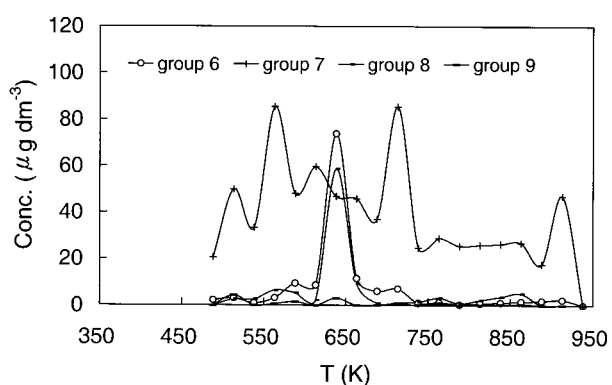


Fig. 4. Variations of instantaneous concentrations of hydrocarbons (groups 6 - 9) at reaction temperature (T).

group 7 (levoglucosan), respectively. The percentages of group 9 (fluouanthene, pyrene, benzo(a)-anthracene, and chrysene) was 0.78%, much lower than that of newspaper pyrolysis (3.32%) [26]. This could possibly be ascribed to the discrepancy of composition of newspaper (mechanical pulp) and toilet paper (chemical pulp). Levoglucosan was the major compound of hydrocarbons. The yields of non-hydrocarbons and of hydrocarbons were about 9.6% and 0.94% at 623 K, 32.59% and 1.71% at 700 K, 58.04% and 1.94% at 788 K, and 88.77% and 2.55% at 938 K, respectively. The results indicated that the non-hydrocarbons were the major pyrolysis products.

In view of the principal components of toilet paper, cellulose is composed of d-glucose units (C₆H₁₀O₅) bonded together by ether-type linkages called glycosidic bonds [27]. And hemicellulose contains two to four (and occasionally five or six) simpler sugar residues [27]. D-Xylose, d-glucose, d-mannose, d-galactose, 1-arabinose, d-glucuronic acid, and 4-O-methyl-d-glucuronic acid residues constitute the majority of hemicellulose monomers, of which d-xylose (C₅H₁₀O) is the most abundant. The structure of hemicellulose is similar to that of cellulose except that its polymers generally contain 50 to 200 units, fewer than

Table 3. Cumulated mass percents (%) of various products relative to initial samples (dry basis) at certain significant temperatures

Product	623 (K)	700 (K)	788 (K)	938 (K)
H ₂	0.01	0.17	0.25	0.35
CO	1.15	4.88	7.73	12.82
CO ₂	4.44	15.02	28.25	47.31
H ₂ O	4	12.52	21.81	28.29
Group 1	0.02	0.11	0.14	0.4
Group 2	0.03	0.09	0.09	0.12
Group 3	0.12	0.23	0.25	0.33
Group 4	0.22	0.35	0.36	0.38
Group 5	0.03	0.07	0.07	0.08
Group 6	0.07	0.15	0.16	0.17
Group 7	0.39	0.59	0.74	0.92
Group 8	0.05	0.11	0.12	0.13
Group 9	0.01	0.01	0.01	0.02
Non-HCs	9.6	32.59	58.04	88.77
HCs	0.94	1.71	1.94	2.55
Volatiles	10.54	34.3	59.98	91.32
Residues	61.35	13.67	8.13	0.5
Volatiles and residues	71.89	47.97	68.11	91.82
Estimated tara	28.11	52.03	31.89	8.18

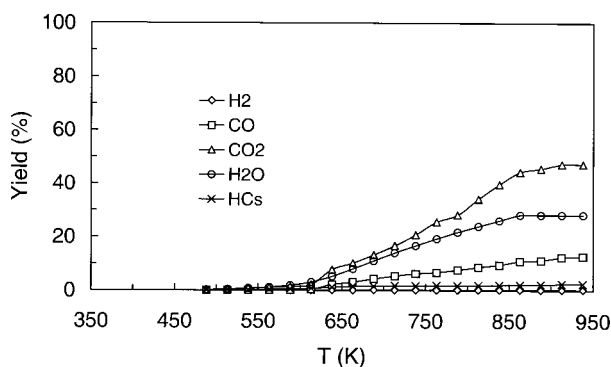


Fig. 5. Yields of major pyrolysis products at various reaction temperatures (T).

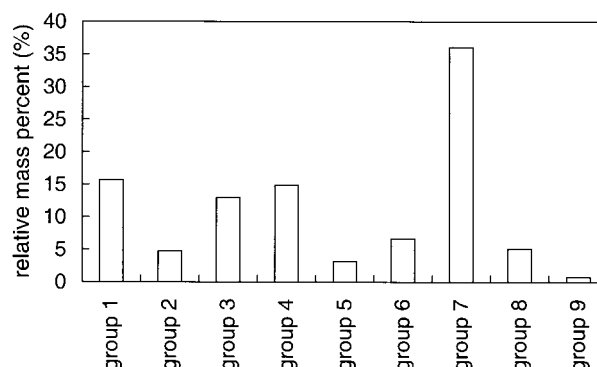


Fig. 6. Percents of groups 1-9 relative to total mass of hydrocarbons.

those of cellulose, and exhibit a branched rather than a linear structure. Hemicellulose is known to be less thermally stable than cellulose. However, the species of the pyrolysis products are similar to those of cellulose, i. e. H₂O, CO, CO₂, acetic acid, furfural, and levoglucosan, etc [9]. In this study, the composition of gaseous products (H₂, CO, CO₂, low-molecular mass compounds) is similar to that of cellulose pyrolysis at atmospheric pressure [9]. According to the literatures [14, 15, 28], the cellulose can be decomposed via two competitive reactions: a dehydration reaction to form anhydrocellulose and a depolymerization reaction to levoglucosan at low temperature range (< 573 K). In a higher temperature range, anhydrocellulose later are decomposed to char and gas via two competitive reactions to form volatiles/intermediates, and gas/char, respectively. Levoglucosan are decomposed to volatiles and char. In our present study, the peak concentrations of levoglucosan were at 563 and 713 K (shown in Fig.

4). According to the pyrolysis mechanisms of cellulose by Mok and Antal [28], the levoglucosan released at 563 K might be ascribed to the depolymerization (primary reaction) of cellulose. Also, the purge gas flow rate and the pressure in the system might affect the secondary reactions and result in different product distribution [29]. The peak concentrations at 713 K might be contributed by the pyrolysis reaction of the other components in toilet paper or by the effects of the purge gas flow rate and pressure in the system, which needs to be explored by a further study.

Mass Balance

The mass percents of residues and cumulated pyrolysis products at various reaction temperatures, as shown in Fig. 7, were obtained by the two-reaction model [18,21] and in this study. According to our previously proposed model [18,21], the decrease of the

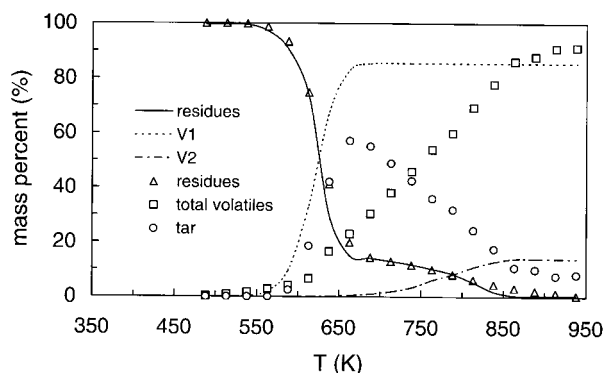


Fig. 7. Mass percents of residues and cumulated products at various reaction temperatures (T). Line: computed; symbol: experimental.

residual mass percent at the first reaction stage (below 660 K) was about 85.5%. However, the cumulated mass of the gases was only 16.59% at 638 K. One might reasonably assume that the V_1 (in two-reaction model) released at this stage consisted of volatiles and liquid tar. The instantaneous and cumulated volatiles quantities were directly obtained from the sampling site. The amount of liquid products (tar) can be estimated from the balance of the experimental quantities of solid residues and volatiles. This then gave the distributions of solid residues, liquid products (tar), and volatiles at different temperatures as illustrated in Table 3 and Fig. 7. The maximum rate of tar released occurred at about 663 K. It was further pyrolyzed to light components in a higher temperature range. The similar results were obtained for the rapid pyrolysis of cellulose [30] and milled wood lignin [31]. However, the maximum rate of tar released occurred at about 873 K in their studies. Since the major components in toilet paper cellulose, hemicellulose with a fraction of impurities, solid residues at the end of the first stage pyrolysis might consist of inorganics, char (primary and secondary char), and remaining hydrocarbons. According to the pyrolysis mechanisms of cellulosic materials [11] and cellulose [28], the primary char with a strong structural integrity is formed following the decomposition of anhydrocellulose. The secondary char with a loose structure was formed by the depolymerization of levoglucosan. In the second stage reaction (> 660 K), the decrease of the residual mass percent was about 14%. The V_2 (in two-reaction model) were the major products. The product distributions were also determined in this study, listed in Table 3 and shown in Figs. 2-6. It was noted that the mass percent of the total volatiles from the experimental work was equal to the summation of the masses of V_1 and V_2 based on the proposed model [18,21]. The solid char formed in the first stage pyrolysis continued to then became more aromatic as the temperature increased. According to the results of the experiments using the pyrolysis of cellulosic materials [11], free

radicals were formed in abundance and thermal cracking proceeded above 623-673 K. Elimination of substituents/bridges and dehydrogenation resulted in forming the polycyclic aromatic clusters. Elimination of oxygen contained in the char occurred simultaneously with the bulk of the hydrocarbon evolution. Elimination of CO, CO₂, H₂O, and oxygenated aromatics and aliphatics might be part of the process of making aromatic hydrocarbons. PAHs were formed in and evolved from solid char during 673 to 873 K, even beginning as low as 623 K for cellulose [11] and 488 K for toilet paper in this work. The results from the study on the pyrolysis of cellulosic materials by Hajalogaol [11] are much similar to this work and supported by the elemental and pyrolysis products analyses. Our results shown in Fig. 7 indicated that the two-reaction model had a good agreement with the experimental data for the pyrolysis of waste toilet paper.

CONCLUSIONS

Pyrolysis experiments of the toilet paper were carried out in a TGA reaction system at a constant heating rate of 5 K min⁻¹ and in a nitrogen environment. The pyrolysis products and the residues were collected and analyzed with gas chromatography and elemental analysis, respectively. The major pyrolysis products investigated included non-hydrocarbons (H₂, CO, CO₂, and H₂O) and hydrocarbons (C₁ - C₃, C₄, C₅, C₆, 1-ring, C₁₀ - C₁₂, levoglucosan, C₁₃ - C₁₅, and C₁₆ - C₁₈). The cumulated masses and the instantaneous concentrations of pyrolysis products were obtained under the experimental conditions. Since the synthetic gases (CO, CO₂, H₂O, HCs) contained a high calorific value, their use as marketable fuels greatly supports the importance for resource recycling of the waste toilet paper according to the observations we made in this study.

ACKNOWLEDGEMENTS

We express our sincere thanks to the National Science Council of Taiwan for the financial assistance under project NSC 88-2211-E-212-001 and also would like to thank the Kimberly-Clark Co., Ltd. (Taiwan), for providing the toilet paper sample.

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Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-chief within six months.

Manuscript Received: August 2, 2002

Revision Received: December 12, 2002

and Accepted: January 17, 2003

實驗室規模之熱重量分析反應器中廢衛生紙熱解產物分佈

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關鍵詞：衛生紙、熱裂解產物、熱重量分析

摘 要

廢衛生紙為臺灣地區都市垃圾主要成分之一。由於衛生紙熱值很高，以熱裂解法將之轉變為有商業價值之燃料，具經濟及環境意義。本研究以實驗室規模之熱重量分析反應器(TGA)熱解廢衛生紙。熱裂解實驗係在氮氣中進行，並控制加熱速率在 5 K min^{-1} 。熱裂解產物及殘餘物收集後，分別以氣體層析儀(GC)及元素分析儀分析之。研究結果顯示，主要產物包括非碳氫化合物類(H_2 , CO , CO_2 和 H_2O)和碳氫化合物類(C_{1-3} , C_4 , C_5 , C_6 , 1-ring, C_{10-12} , levoglucosan, C_{13-15} 和 C_{16-18})。產物之累積質量及濃度亦從實驗結果中獲得。主要產物之產率分別為 0.35% H_2 、12.82% CO 、47.31% CO_2 、28.29% H_2O 及 2.55% 碳氫化合物類。左旋失水葡萄糖(levoglucosan)為碳氫化合物類主要成分。焦油(tar)在不同熱裂解溫度下之預估值，可由相關實驗數據計算獲得。本研究結果對廢衛生紙熱裂解程序設計，及其熱裂解機制之了解有所幫助。