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Study on pyrolysis of typical medical waste materials by using TG-FTIR analysis

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Abstract

Pyrolysis of certain medical waste materials was studied using thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR). Pyrolysis characteristics of three common materials were discussed. The pyrolysis of absorbent cotton turned out to be the most concentrative, followed by medical respirator and bamboo stick. From TG and DTG curves, pyrolysis of these three materials occurred in single, two and three stages respectively. Evolved volatile products from all these three materials included 2-butanone, benzaldehyde, formic acid, acetic acid, hydrocarbon, carbon dioxide, carbon monoxide, and water; whereas no sulphur dioxide, ammonia and hydrogen cyanide was detected. There are several differences in yield among them. However, the study in this paper is essential for medical waste pyrolysis model, the TG-FTIR approach is potential to provide valuable inputs for predictive modeling of medical waste pyrolysis. More studied are needed to get the kinetic parameters and pyrolysis models that can predict yields and evolution patterns of selected volatile products for CFD applications.

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Keywords: Medical waste; Pyrolysis; TG-FTIR analysis

1. Introduction

Medical waste, if not treated properly, may be hazardous to both people and environment. As the incineration of medical waste is underdeveloped in China, it is important to know the products during pyrolysis and incineration. Although the composition of medical waste is quite complex, several materials are always included, such as absorbent cotton, medical respirator and bamboo stick. Among current technologies, incineration has been found to be widely, the most important advantage of incineration is that it significantly reduces the volume of material, destroys pathogens and hazardous organics, and renders the waste unrecognizable materials in the form of ash. Additionally, incineration is predicted to be more popular in the future in China. Medical waste incineration plant refers not just to the mass burn, but also to any type of thermal treatment systems for discarded materials that waste resources and generate pollutants. These include systems based upon combustion, pyrolysis, and thermal gasification. So it is necessary to analyze the pyrolysis characteristics of medical wastes.

Pyrolysis plays an important role in combustion processes due to the tremendous diversity of medical waste sources. It is important to build comprehensive medical waste pyrolysis models that can predict product specification and yields. However, few detailed products information on medical waste pyrolysis was found in the available literature. The lack of data, combining with the large variety and complexity of medical wastes, leads to difficulties in understanding emission behavior of medical wastes during the thermal treatment process. Medical waste pyrolysis characteristics can be clarified after pyrolysis of each medical waste is studied.

TG is used widely in thermal analysis and kinetics parameters study under both nitrogen and air atmospheres [1–4]. For pyrolysis, different heating rates are carried out to obtain the kinetic model. For combustion, different oxygen concentrations and heating rates are taken into account by using TG. But the composition of evolved gas in each weight loss steps cannot be observed only by using TG. On other hand, Fourier transform infrared spectroscopy (FTIR) results can be used to evaluate the

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functional groups and prove the existence of some emissions [5,6]. FTIR, which provides plenty of information of mixed gases, can be used to identify the composition of mixture, as well as be used to quantify CO_2, CO, CH_4, C_2H_2, C_2H_4, HCN and NH_3, etc. [7,8].

TG combining with FTIR is a useful tool in dynamic analysis as it monitors continuously both the time dependent evolution of the gases and the weight of the non-volatile materials (residue). It has already been used widely to investigate biomass pyrolysis [9–11] and polymers thermal degradation [12,13], as well as to forecast the hazardous emissions that may be produced in the case of major accidents [14]. But very limited studies were conducted using TG combining with FTIR on medical wastes.

In this study, volatile products from TG during TG-FTIR experiment were swept into gas cell immediately by carrier-gas so that secondary reactions were minimized. At the same time, 3D spectrum that reflects the effect of time and wavenumber was generated by Nicolet spectrometer. The results of weight loss and composition of evolved gases obtained through the study, provide plentiful information to understand the pyrolysis characteristics of medical wastes.

2. Experimental materials and method

2.1. Experiment materials

Absorbent cotton, medical respirator and bamboo stick were chosen as experiment materials for they are popular in medical wastes. In order to make the sample heated sufficiently, we split medical respirator to small pieces (square of 1 mm) and grinded bamboo stick to powder (diameter is less than 100 μm) before conducting experiment. The small sample size used in this work ensured that temperature gradients within the sample were minimized. All samples were dried in oven at 105 °C for 3 h, so the moisture of sample was removed to minimize the interaction in the pyrolysis phase of particle conversion. The results of elemental analysis of samples were shown in Table 1.

2.2. Experiment method

The Nicolet Nexus 670 spectrometer and Mettler Toledo TGA/SDTA851^e thermo analyzer were coupled by a Thermo-Nicolet TGA interface model, of which the stainless transfer line and gas cell (20 cm path length) were set to 180 °C to minimize the change of evolved gas. Nitrogen was used as the purge gas for both TGA and spectrometer. Resolution in FTIR was set as 4 cm^{-1}, number of scans per spectrum was set as 20 times/min, and the spectral region was set as 4000–400 cm^{-1}.

The TG curve is similar with the heating rate from 10 °C/min to 50 °C/min, and the temperature for the maximum rate of weight loss shifts to higher temperature levels as the heating rate increases, but the temperature increases less than 20 °C, thus the optimization experiment conditions were as follows: nitrogen atmosphere with a flow rate of 30 ml/min, heating rate of 30 °C/min, temperature from 30 °C to 960 °C. Because the evolved gas could be swept into the gas cell immediately after they are formed, the slower the purge flow selected, the higher the sensitivity expected. Flow rate of the purge gas was set also 30 ml/min. To FTIR, a weight loss about 10 mg usually gives adequate signal, so approximately 12 mg of samples was used in this study. Medium-sized crucible of 70 μL made of Al_2O_3 was adopted as the sample container.

3. Results and discussion

3.1. TG and DTG analysis

TG and DTG curves were shown in Fig. 1(a–c), it shows that curves are similar when the temperature is lower than 200 °C or higher than 520 °C. However, from 200 °C to 520 °C, pyrolysis processes are different due to different materials. For absorbent cotton, the DTG curve exhibits a single peak at 384 °C. For medical respirator, there are two pyrolysis peaks at 381 °C and 494 °C. For bamboo stick, pyrolysis occurs in three stages, the DTG peak temperatures are 313 °C, 363 °C and 494 °C respectively. The weight loss start temperature (T_s) is: $T_{\mathrm{s,bamboo\ stick}} < T_{\mathrm{s,medical\ repirator}} < T_{\mathrm{s,absorbent\ cotton}}$. The weight loss finish temperature (T_f) is: $T_{\mathrm{f,bamboo\ stick}} > T_{\mathrm{f,medical\ repirator}} > T_{\mathrm{f,absorbent\ cotton}}$. So the temperature range ($\Delta T = T_f - T_s$) for thermal decomposition is: $\Delta T_{\mathrm{bamboo\ stick}} > \Delta T_{\mathrm{medical\ repirator}} > \Delta T_{\mathrm{absorbent\ cotton}}$. It indicates that the pyrolysis of absorbent cotton is the most concentrative, followed by medical respirator and bamboo stick. To absorbent cotton, all products evolve at one stage; to medical respirator and bamboo stick, products evolve at two and three stages respectively.

The final weight loss of the absorbent cotton, medical respirator and bamboo stick are 10.81%, 11.43% and 17.91% respectively. The residual char and ash in proximate analysis of these three materials is absorbent cotton < medical respira-

Table 1
Proximate and ultimate analysis of materials

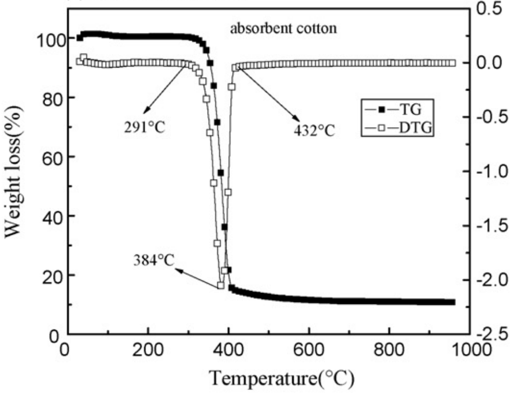
Material	Proximate analysis (%)				Ultimate analysis (%)					Q_{HHV} (MJ/kg)
	Moisture[a]	Ash[b]	Volatiles	Fixed carbon	C	H	O	N	S	
Cotton	6.46	0.20	96.40	3.60	44.92	9.00	45.86	0.19	0.03	15.789
Respirator	7.01	4.14	92.47	7.53	51.28	6.69	41.71	0.18	0.14	18.103
Bamboo stick	9.77	1.96	82.17	17.83	50.76	5.91	42.98	0.28	0.07	17.446

Unless stated otherwise, all data are expressed in weight percent on a dry, ash-free basis. Oxygen content was determined by difference.

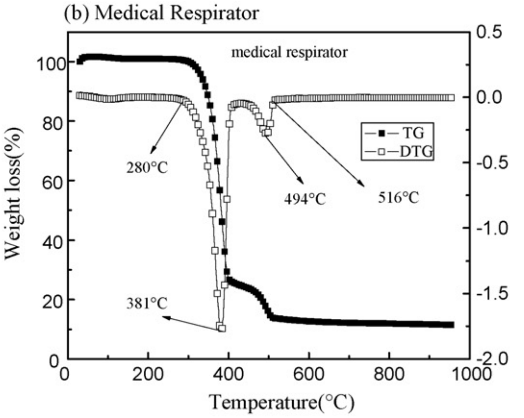
[a] As-received basis.

[b] Dry basis.

(a) Absorbent Cotton



(b) Medical Respirator



(c) Bamboo Stick

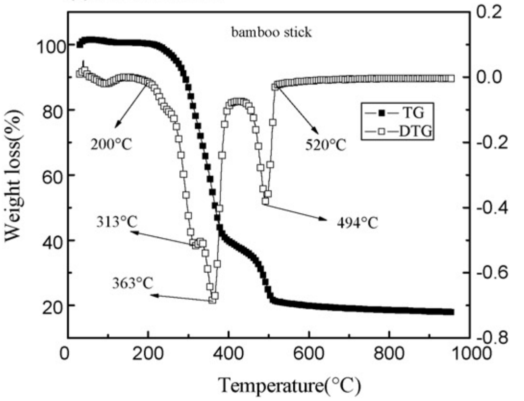


Fig. 1. Curve of TG and DTG for materials (heating rate of 30 °C/min).

tor < bamboo stick. So the final weight loss has relation with the residual char and ash. The differences in TG curve may be caused by different volatile and moisture contents in each material.

3.2. FTIR analysis

Infrared spectrum is often used to distinguish the various inorganic and organic compounds from pyrolysis. The 3D infrared spectrum of evolution gases includes information of infrared absorbance, wavenumber and temperature. From the infrared spectrum, the change of spectral intensity along time direction is similar to TG results, for absorbent cotton, there is a single intensity peak; for medical respirator, there are two intensity peaks; for bamboo stick, there are three intensity peaks. But the temperature at the spectral intensity peak is decided by TG because there are several seconds delay from TG to FTIR.

3.2.1. Analysis of gas composition

After evolved gases from TG were swept into the gas cell, absorbance information at different wavenumber and different

Table 2
Identification of molecule configuration

Wavenumber(cm^{-1})	Peak (cm^{-1})	Functional group	Vibration	Product
3500-4000	3566.7	O-H	stretch	H_2O
1275-1875	1507	H-O-H	bending	
2402-2240	2368.53	C=O	stretch	CO_2
736-605	669.15	C=O	stretch	
2240-2060	2171.43	C-O	stretch	CO
2240-2060	2112.48	C-O	stretch	
3115-2675	2819	-C-H	stretch	ketone
1855-1600	1735	C=O	stretch	
3115-2675	2819	-C-H	stretch	aldehyde
1855-1600	1720	C=O	stretch	
3400-3600	3566.70	O-H	stretch	acid
1860-1650	1774	C=O	stretch	
1300-1000	1180	C-O	stretch	
3115-2675	2819	-C-H	stretch	hydrocarbon
1500-1300	1506.98	-C-H	bending	
1300-1000	1095	C-O/C-N	stretch	ether/amine

time can be obtained by Fourier transform. When the time is fixed, absorbance information at different wavenumber can be obtained to analyze the composition of gases at this moment; at the same time, when the wavenumber is fixed, absorbance information at different time can also be obtained under this wavenumber to analyze the certain component as a function of time.

Here we take the first spectral intensity peak of bamboo stick for example. *First*, fixing the time according to maximum spectral intensity, most gases evolve at that time. The spectrum includes two parts: the spectrum in functional groups region (4000–1333 cm^{-1}), in which the absorption is conspicuous, the other part is fingerprint region (1333–667 cm^{-1}), in which the absorption is less conspicuous. *Second*, we establish preliminary identification of functional groups that exist in the spectrum. Main wavenumber corresponding to the functional groups is shown in Table 2. *Third*, we check the library in OMNIC and find possible species in the library, pay attention to large and conspicuous peaks of each species spectrum, then compare the experiment spectrum with the standard species spectrum, also check the absorption band at fingerprint region of the spectrum. *Fourth*, some compounds such as CO_2 and CO can be identified directly, we separate the known compounds by subtracting them from the mixture spectrum. That is to say, the mixture spectral is the sum of the spectra of all components. A certain time is selected in Gram-Schmidt to get the spectral at this time; then a reference spectra of know species is chosen from the library which constitutes a database of reference spectra collected over years by applying the TG-FTIR technique, the reference spectra is opened. After that, these two spectra (sample spectra at certain time and reference spectra) are selected, spectral math (or subtract) is chosen from the process menu. When the spectral math window appears, with the sample spectrum at the top and the spectra of reference spectra below it, the $A - K \times B$ operation is selected, the value of K (scaling factor) later can be adjusted by subtracting the reference spectra. By subtracting a spectrum of a pure component from the sample spectrum, it provides a simpler mixture spectrum. For different possible components, it can be subtracted other reference spectra from the simpler mixture spectral. Once this is done, features from the spectrum will be read very easily.

Combined with the 3D spectrum, main products are identified as follows: CO_2, CO, H_2O, acid such as formic acid and acetic acid, aldehyde such as benzaldehyde, ketone such as 2-butanone, also hydrocarbon. The hydrocarbons have many branches because the spectral intensity is equal at 1460 cm^{-1} and 1380 cm^{-1}, at the same time there is absorbance at 880 cm^{-1}, which means the phenyl also exists. To ether, its IR characteristic is not unique, whether it exists or not is not sure. The absorbance of ketone, acid and hydrocarbon is strong and the N takes part of little proportion in element analysis, so the absorbance of N-product is not enough to be distinguished. There is no conspicuous absorbance in 3400–3200 cm^{-1}, 1700–1500 cm^{-1}, 1000–900 cm^{-1}, which means very little or no HCN evolved. There is no conspicuous absorbance in 3400–3200 cm^{-1} and 800–600 cm^{-1}, which means very little or no NH_3 evolved. At the same time, there is no absorbance in 3400–3200 cm^{-1}, so no N–H compounds evolved. The possible N-product is amine without N–H configuration. But on the one hand, HCN and HNCO were found to be the major N-Products, while the NH_3 fraction was detected to a minor extent in wood pyrolysis [9], and appreciable difference in product yields for hold times longer than 10 s observed only for the species that require harsher pyrolysis conditions for their release, e.g. HNCO, and to lesser extent also HCN in tobacco pyrolysis [11]. On the other hand, no HCN and NH_3 presented in biomass pyrolysis [7]. In this study, the

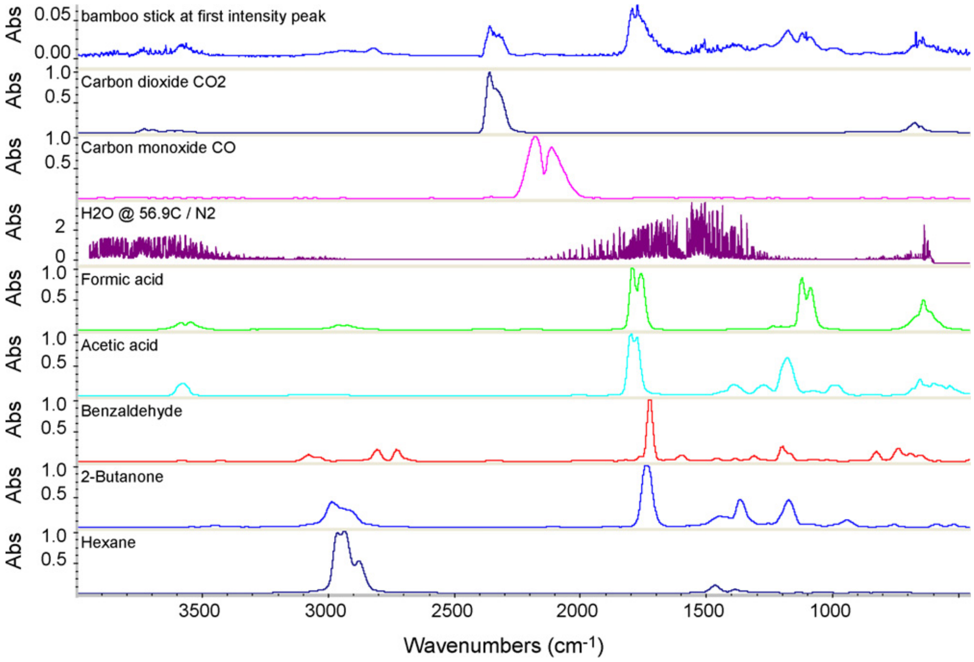


Fig. 2. Identification of bamboo stick pyrolysis at first DTG peak (319 °C).

evolved of NH_3 and HCN is either in small amount that cannot be detected or none of them evolved. To S-product, the functional group is 1500–1000 cm^{-1}, which overlap with C–H, C–O stretching, there is no other conspicuous band position, and the S takes part of little proportion in element analysis, so whether SO_2 exists or not is also not sure. In fact, the number of evolved products can be numerous, not all of the products can be identified or separated from each other. In addition, gases like H_2, N_2, O_2, cannot be detected by means of FTIR due to the absence of a dipole, H_2S has its main peaks below the CO_2 peaks and CO_2 is present in a much larger quantity than H_2S, so H_2S is impossible to be detected [10]. Some evolved volatile products of bamboo stick pyrolysis at first DTG peak is shown in Fig. 2.

3.2.2. *Differences of evolution gas*

After the composition of pyrolysis product was identified, the distribution of each product against time and temperature can be obtained. The TG-FTIR pyrolysis product evolution patterns for bamboo stick, absorbent cotton and medical respirator are overlaid in Fig. 3. The curves in Fig. 3 for the three samples are plotted as a function of temperature, the analysis of the evolution patterns shown in Fig. 3 leads to the following observations:

- The evolution patterns of each of the following species were found to be similar for absorbent cotton and medical respirator: aldehyde, ketone, acid, CO_2, CO.

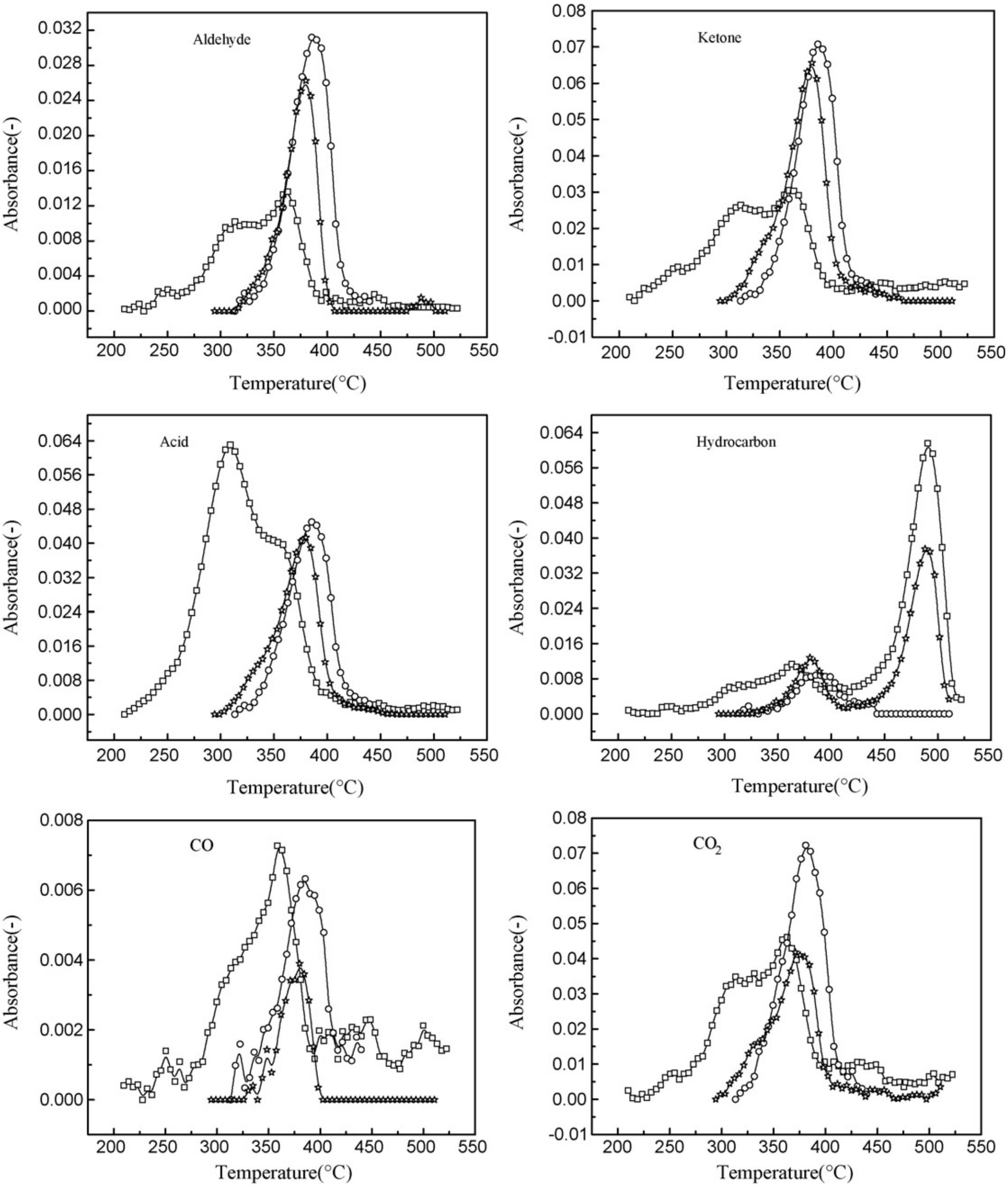


Fig. 3. Comparison of TG-FTIR pyrolysis product evolution pattern for bamboo stick (□), absorbent cotton (○), and medical respirator (☆).

- To absorbent cotton, all products evolve at the same time.
- To medical respirator, ketone, aldehyde, acid, CO_2, CO and little hydrocarbon evolve at first stage, and most of hydrocarbon evolves at second stage.
- To bamboo stick, most of aldehyde, ketone, acid, CO and CO_2, also little hydrocarbon evolve at first stage, but most of hydrocarbon and a few of aldehyde, ketone, acid, CO and CO_2 evolve at the next stage.
- Absorbent cotton has no high-temperature hydrocarbon peak.
- Absorbent cotton and medical respirator have a larger aldehyde and ketone peak than does bamboo stick. But the bamboo stick has a larger acid peak than absorbent cotton and medical respirator.
- Bamboo stick and medical respirator have a larger hydrocarbon peak than absorbent cotton.
- Absorbent cotton has a larger CO_2 and CO peak than medical respirator.
- In all three samples, the absorbance of ketone is more than the absorbance of aldehyde, bamboo stick displays earlier evolution of all species than absorbent cotton and medical respirator.

The comparison of Figs. 4 and 5 leads to the following observations:

- The pyrolysis of bamboo stick takes place at low temperature than absorbent cotton and medical respirator.

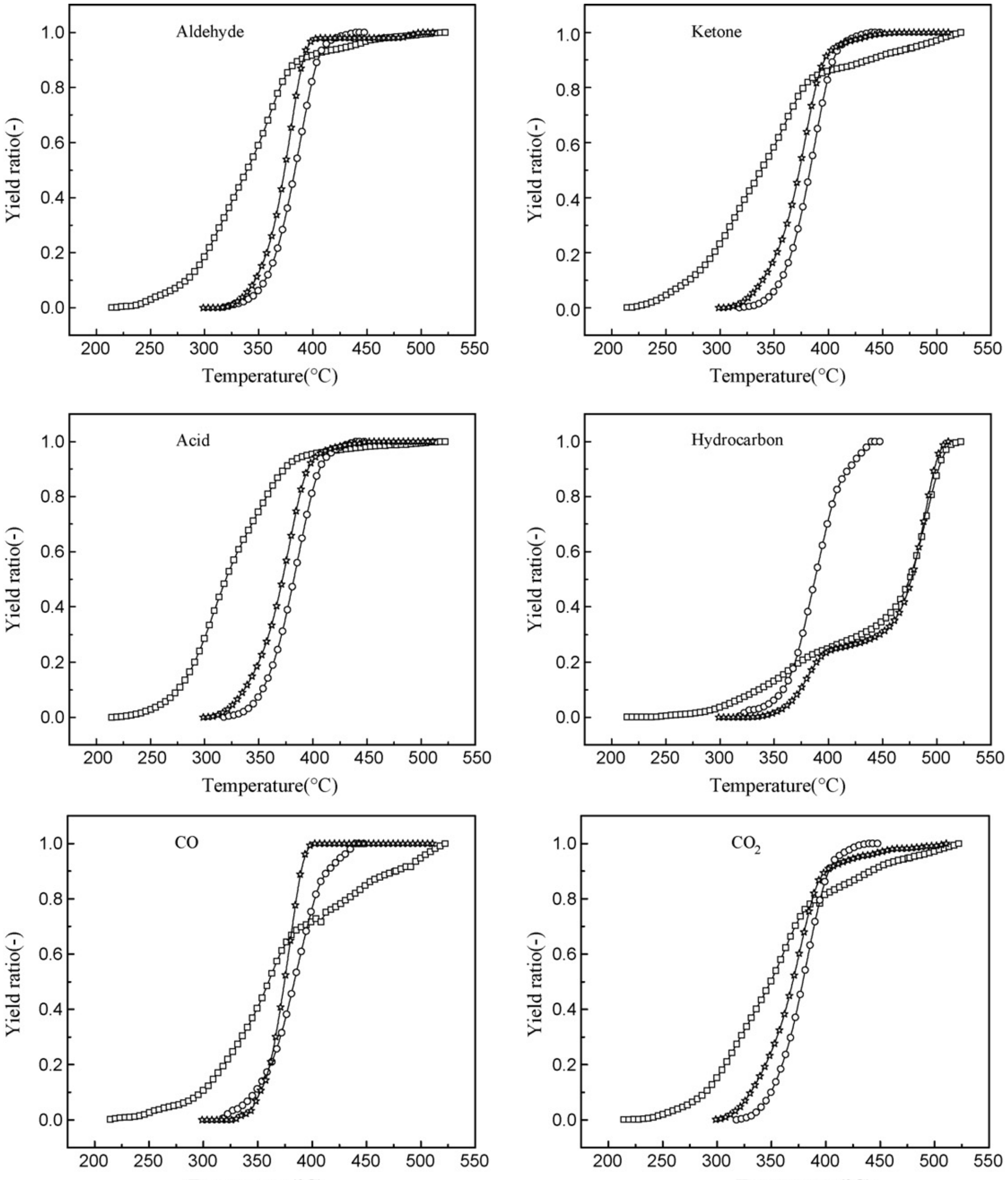


Fig. 4. Comparison of yield ratio for each pyrolysis product from TG-FTIR analysis for bamboo stick (□), absorbent cotton (○), and medical respirator (☆).

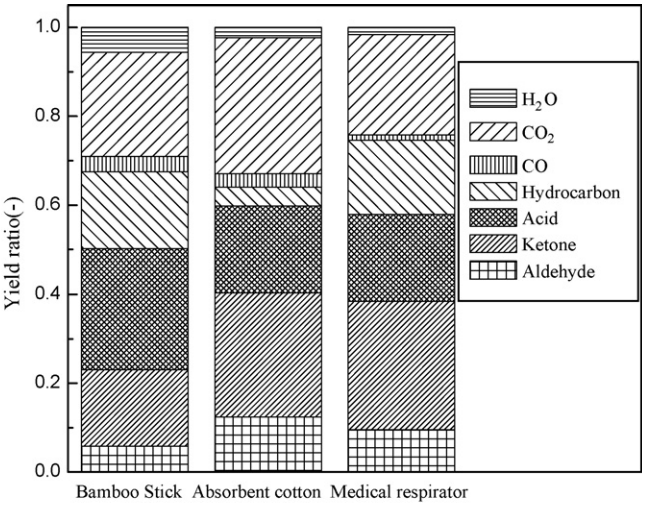


Fig. 5. Comparison of yield ratio of all pyrolysis products from TG-FTIR analysis.

- Most of the evolution of gases of medical respirator occurs at low temperature than that of absorbent cotton, exception of hydrocarbon and CO.
- Medical respirator and bamboo stick exhibit more complex hydrocarbon evolution pattern than absorbent cotton.
- In the case of ketone, aldehyde, hydrocarbon, CO, CO_2, bamboo stick seems to evolve from low temperature to high temperature, but the low temperature evolution is stronger than the high temperature evolution.

In addition, the following observations are made:

- The yield ratio of CO_2 for absorbent cotton is more than that of bamboo stick and medical respirator.
- The yield ratio of CO is low for all three materials, and medical respirator has the least yield ratio of CO among them.
- Bamboo stick and medical respirator have higher yield ratio of hydrocarbon than absorbent cotton.
- Bamboo stick has the highest yield ratio of acid among them.
- Absorbent cotton has the highest yield ratio of ketone and aldehyde among them.

4. Conclusions

Three common medical waste materials (absorbent cotton, medical respirator and bamboo stick) were studied. We successfully analyzed the pyrolysis process and evolved gases by using TG-FTIR. But the study here is only based on qualitative analysis. Our work in this paper is essential for medical waste pyrolysis models. TG-FTIR approach is potential to provide valuable inputs for predictive modeling of medical waste pyrolysis. Further study is planned. First, TG-FTIR pyrolysis experiments will carry out at several heating rates and the results will be used to determine kinetic parameters for a pyrolysis model based on parallel, independent, first-order reactions with Gaussian distribution of activated energies [11]. Then the Distributed Activation Energy Model (DAEM) model [15] would be used to solve the yield and rate of evolution for individual pyrolysis product with given kinetic parameters from TG-FTIR analysis. The rates of yield of species are used as source terms in the species transport equations in CFD simulation, the understanding of the evolution of volatile species during medical waste pyrolysis and CFD simulation are valuable for understanding and improving the medical waste incineration.

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