



## Analysis of volatile species kinetics during typical medical waste materials pyrolysis using a distributed activation energy model

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### ABSTRACT

The complex reactions of typical medical waste materials pyrolysis and the evolution of different volatile species can be well represented by a Distributed Activation Energy Model (DAEM). In this study, A thermogravimetric analyser (TGA), coupled with Fourier transform infrared analysis of evolving products (TG-FTIR), were used to perform kinetic analysis of typical medical waste materials pyrolysis. A simple direct search method was used for the determination of DAEM kinetic parameters and the yield of individual pyrolysis products under any given heating condition. The agreement between the model prediction and the experimental data was generally good. The results can be used as inputs to a pyrolysis model based on first-order kinetic expression with a Gaussian Distribution of Activation Energies as a sub-model to CFD code.

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### 1. Introduction

Medical waste, if not treated properly, may be hazardous to both people and the environment. As the incineration of medical waste is underdeveloped in China and other countries, the understanding of the evolution of volatile species during medical waste pyrolysis is important for improving incineration plant design and control for medical waste incineration. But the process of medical waste incineration is a very complex phenomenon involving heating-up, pyrolysis, oxidation of the volatiles and chars, multiple reactions and complicated flow fields. In a reductive atmosphere, the volatiles may not have a chance to be oxidized. So pyrolysis is an important part of the entire process and due to the tremendous diversity of medical waste feedstocks. However, few detailed model for evolution species in medical waste 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 thermal treatment process for medical wastes. So it is necessary to develop a pyrolysis model to predict the evolution yield during the pyrolysis under different conditions for various medical wastes.

Thermogravimetry (TG) has been widely used in the kinetic analysis and the determination of the kinetic parameters of solid-state reactions [1–3]. However, the kinetic parameters obtained from the TGA data correspond to the overall conversion process,

which differ from the individual kinetic parameters of evolving species during the pyrolysis process. On the other hand, Fourier transform infrared spectroscopy (FTIR) results can be used to evaluate the functional groups and prove the existence of some emissions [4,5]. TG combined with FTIR was a useful tool in dynamic analysis as it continuously monitored 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 material pyrolysis, as well as to forecast the hazardous emissions that may be produced in the case of major accidents [6]. From the TG-FTIR analysis, we could obtain the evolution products and its yield characteristics. Then, the kinetic parameters for each volatile species can be derived.

In the available literatures, Distributed Activation Energy Model (DAEM) has been widely used to analyze complex reactions such as pyrolysis of various ranks of coal and biomass [7–11], as well as used to analyze the evolution of different volatile species during pyrolysis [12,13]. And different methods were used to solve the DAEM model to obtain the kinetic parameters [8,9,14–18]. Miura [8,9] used only three sets of experimental data to obtain both  $f(E)$  and frequency factor  $k_0(E)$ . Günes and Güneş [14] used a simple direct search method for the determination of DAEM kinetic parameters from only one set of experimental data. Thakur and Nuttal [15] and Xiang et al. [16] presented the Marquardt non-linear regression method to establish the kinetic parameters. Cai and Liu [18] developed a new DAEM, which considering the reaction order and the dependence of frequency factor on temperature. And parametric study of the  $n$ th-order Gaussian DAEM and  $n$ th-order Weibull

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DAEM also been performed [19,20]. After the heating rate was specified and kinetic parameters were available, computer codes based on DAEM, such as FG-DVC [21,22] and FLASHCHAIN [23–25], can be used to predict the yield of individual pyrolysis products. Then the product yield predictions can be used as inputs to the CFD combustion code. While combustion and pyrolysis models for coal and biomass were increasing applied in CFD studies, there were few analogous models available for medical waste pyrolysis in CFD computations at the present time. Thus it is greatly needed to obtain the kinetic parameters for medical waste pyrolysis process.

In this study, modeling of volatile species evolution during typical medical waste materials pyrolysis on the basis of thermogravimetric analyser (TGA), coupled with Fourier transform infrared analysis of evolving products (TG-FTIR) data is presented. As well, a direct search method for the determination of Gaussian Distribution of Activation Energies kinetic parameters is presented. After the kinetic parameters were derived, the DAEM model can be coupled with CFD code to get the instantaneous temperature as input and deliver the product yields as outputs.

## 2. Experimental materials and method

### 2.1. Experimental materials

In our previous work [26], absorbent cotton, medical respirator and bamboo stick were chosen as experiment materials since these materials are typical medical wastes. All samples were dried in an oven at 105 °C for 3 h to remove the moisture of the sample to minimize the interaction in the pyrolysis phase of particle conversion. The results of elemental analysis of samples are shown in Table 1.

### 2.2. Experimental method

The Nicolet Nexus 670 spectrometer and Mettler Toledo TGA/SDTA851<sup>e</sup> thermo analyzer were coupled by a Thermo-Nicolet TGA interface model, of which the stainless transfer line and gas cell were set to 180 °C to minimize the change of evolved gas. Samples were heated at 30 °C min<sup>-1</sup> in a nitrogen environment, the volatile products were swept immediately into the gas cell, which minimized secondary reactions. Pyrolysis products were analyzed by Fourier transform infrared (FTIR) spectroscopy, resolution in FTIR was set as 4 cm<sup>-1</sup>, and the spectral region was set as 4000–400 cm<sup>-1</sup>. Approximately 12 mg samples were used in the study. A detailed description of the TG-FTIR can be found in the literature [26].

## 3. Theory and method

### 3.1. DAEM equation

To analyze complex reaction, the so-called DAEM has been widely utilized, the model has been applied to represent the change

in overall conversion and/or the change in the yield of a given conversion during coal and biomass pyrolysis. DAEM assumes that the evolution of a given product involves an infinite number of independent chemical reactions. Each reaction contributes to the reaction of a product according to:

$$\frac{dY_i}{dt} = -k_i Y_i \quad (1)$$

where  $Y_i$  refers to the unreacted mass fraction of species  $i$  in the initial material and  $k_i$  denotes the rate constant of the corresponding reaction. The rate constant  $k_i$  typically has Arrhenius form. Integrating Eq. (1) over time and over all reactions with different activation energies distribution  $f_i(E)$ , one obtains the following expression:

$$\frac{Y_i}{Y_{i,0}} = \int_0^\infty \exp\left(-\int_0^t k_i(E) dt\right) f_i(E) dE \quad (2)$$

where  $Y_{i,0}$  is the initial mass fraction of species  $i$  in the material before pyrolysis starts. Usually,  $f_i(E)$  is taken to be a Gaussian distribution with a mean activation energy of  $E_{i,0}$  and a standard deviation  $\sigma_i$ . hence:

$$f_i(E) = \frac{1}{(\sigma_i(2\pi))^{1/2}} \times \exp\left(-\frac{(E - E_{i,0})^2}{(2\sigma_i^2)}\right) \quad (3)$$

When a sample is heated at a constant heating rate  $H$  from a low temperature  $T_0$ , then the temperature of sample at time  $t$  is given by:

$$T = T_0 + Ht \quad (4)$$

$$\text{Let's define } \Phi(E, T) = \exp\left(-\int_0^t k_i(E) dt\right) \quad (5)$$

Using the Arrhenius form  $k_i$  and  $P(x) = \exp(-x)/x^2$ , Eq. (5) is rewritten as follows [8,14]:

$$\Phi(E, T) = \left(\frac{\exp(-(k_{i,0}RT^2))}{(HE) \times \exp(-E/(RT))}\right) \quad (6)$$

Using Eqs. (3) and (6), one may express Eq. (2) for the yield as:

$$\frac{Y_i}{Y_{i,0}} = \frac{1}{(\sigma_i(2\pi))^{1/2}} \times \int_0^\infty \exp\left(\frac{-k_{i,0}RT^2}{(HE)}\right) \times \exp\left(\frac{(-E/(RT)) - (E - E_{i,0})^2}{(2\sigma_i^2)}\right) dE \quad (7)$$

Eq. (7) is the final equation from this paper for obtaining the kinetic parameters of typical medical waste materials pyrolysis and modeling of volatile species evolution during typical medical waste materials pyrolysis.

**Table 1**  
Proximate and ultimate analysis of materials

Material	Proximate analysis (%)				Ultimate analysis (%)					$Q_{HHV}$ (MJ/kg)
	Moisture <sup>a</sup>	Ash <sup>b</sup>	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.

<sup>a</sup> As-received basis.

<sup>b</sup> Dry basis.

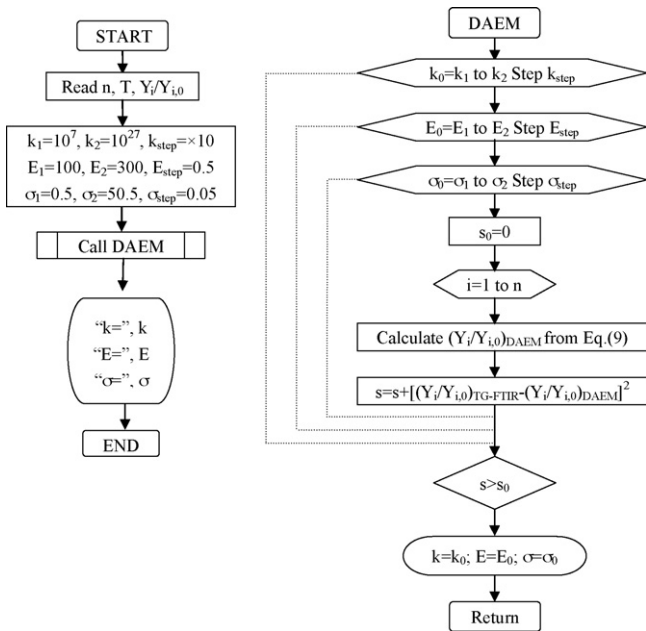


Fig. 1. The block diagram of computer program.

### 3.2. Numerical solution of DAEM equation

There are some mathematical difficulties in the determination of the Gaussian DAEM kinetic parameters due to the structure of the DAEM equation. The structure of DAEM equation also causes many difficulties in the use of general purpose curve fitting softwares. In the previous studies, these parameters were established using methods such as (1) non-linear Hooke and Jeeves optimizing method [17]; (2) Marquardt non-linear regression method [15,16]. (3) and  $T_{\max}$  method [8,9,12]. In the  $T_{\max}$  method, some difficulties can be encountered when peaks are not well resolved, in which cases substantial shifts in  $T_{\max}$  can occur. The exact value of  $T_{\max}$  may also be difficult to determine for large, broad peaks. (4) Search method, Cai and Ji [27] presented a pattern search method and Güneş and Güneş [14] presented a direct search method to determine the DAEM kinetic parameters from the TGA data of coals and the frequency factor was assumed to be constant at  $1.67 \times 10^{13} \text{ s}^{-1}$ . In this study, a direct search method to be used for the determination of DAEM kinetic parameters from the TG-FTIR data of typical medical waste materials is presented. A computer program using C++ has been written to perform the numerical solution of Eq. (7) and the Simpson's 1/3 rule has been used for integration. The block diagram of this computer program is given in Fig. 1.  $E_0$  values were between 100 and 300 kJ/mol, obtained value for  $\sigma$  was between 0.5 and 50.5 kJ/mol, also value for  $k_0$  was between  $10^7$  and  $10^{27}$ . Under certain  $k_0$ ,  $E_0$  and  $\sigma$ ,  $Y_i/Y_{i,0}$  from Eq. (7) can be solved for each reac-

Table 2

Kinetic parameters ( $k_0$ ,  $E_0$  and  $\sigma$ ) and correlation coefficients ( $r$ ) for absorbent cotton pyrolysis

Species	$T$ (K)	$k_0$ ( $\text{s}^{-1}$ )	$E_0$ ( $\text{kJ mol}^{-1}$ )	$\sigma$ ( $\text{kJ mol}^{-1}$ )	$s$	$r$
CO	586–713	$1\text{e}+15$	188.5	4.2	0.001662	0.998
CO <sub>2</sub>	586–713	$1\text{e}+20$	248.0	5.2	0.000967	0.992
H <sub>2</sub> O	586–713	$1\text{e}+21$	260.5	1.2	0.000645	0.997
Hydrocarbon	586–713	$1\text{e}+23$	289.0	8.0	0.001817	0.984
Aldehyde	586–713	$1\text{e}+19$	237.5	3.3	0.000581	0.999
Ketone	586–713	$1\text{e}+21$	262.0	4.5	0.000612	0.996
Acid	586–713	$1\text{e}+20$	249.5	5.1	0.000731	0.992

tion. Kinetic parameters searched for the sample will be  $k_0$ ,  $E_0$  and  $\sigma$  values where  $s$  is minimized in all conditions.

$$s = \sum_{j=1}^n \left( \left( \frac{Y_i}{Y_{i,0}} \right)_{\text{TG-FTIR}} - \left( \frac{Y_i}{Y_{i,0}} \right)_{\text{DAEM}} \right)^2 \quad (10)$$

where  $n$  is data number in one serial data.  $(Y_i/Y_{i,0})_{\text{TG-FTIR}}$  and  $(Y_i/Y_{i,0})_{\text{DAEM}}$  are experimental value of mass transform fraction from TG-FTIR analysis and calculated value of mass transform fraction from DAEM model.

## 4. Results and discussion

From the direct search method discussed above, Eq. (7) can be used for each species that evolved as a single peak in the TG-FTIR experiment. To identify the volatile species in the TG-FTIR, the follow steps should be took. *First*, we fix the time according to maximum spectral intensity, and divide the spectrum into unique portion and lower-noise portion. *Second*, we establish preliminary identification of functional groups that exist in the spectrum. *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, pay attention to the unique portion and take care of the low-noise portion of the spectrum. *Fourth*, CO<sub>2</sub>; CO and H<sub>2</sub>O can be identified directly, we separate the known compounds by subtracting them from the mixture spectrum. Once this is done, features from the spectrum could be read more easily. Combined with the 3D spectrum, main products can be identified as follows: CO<sub>2</sub>; CO; H<sub>2</sub>O; acid; aldehyde; ketone and hydrocarbon. A detailed description of the procedures used for species identification and data analysis can be found in our previous study [26].

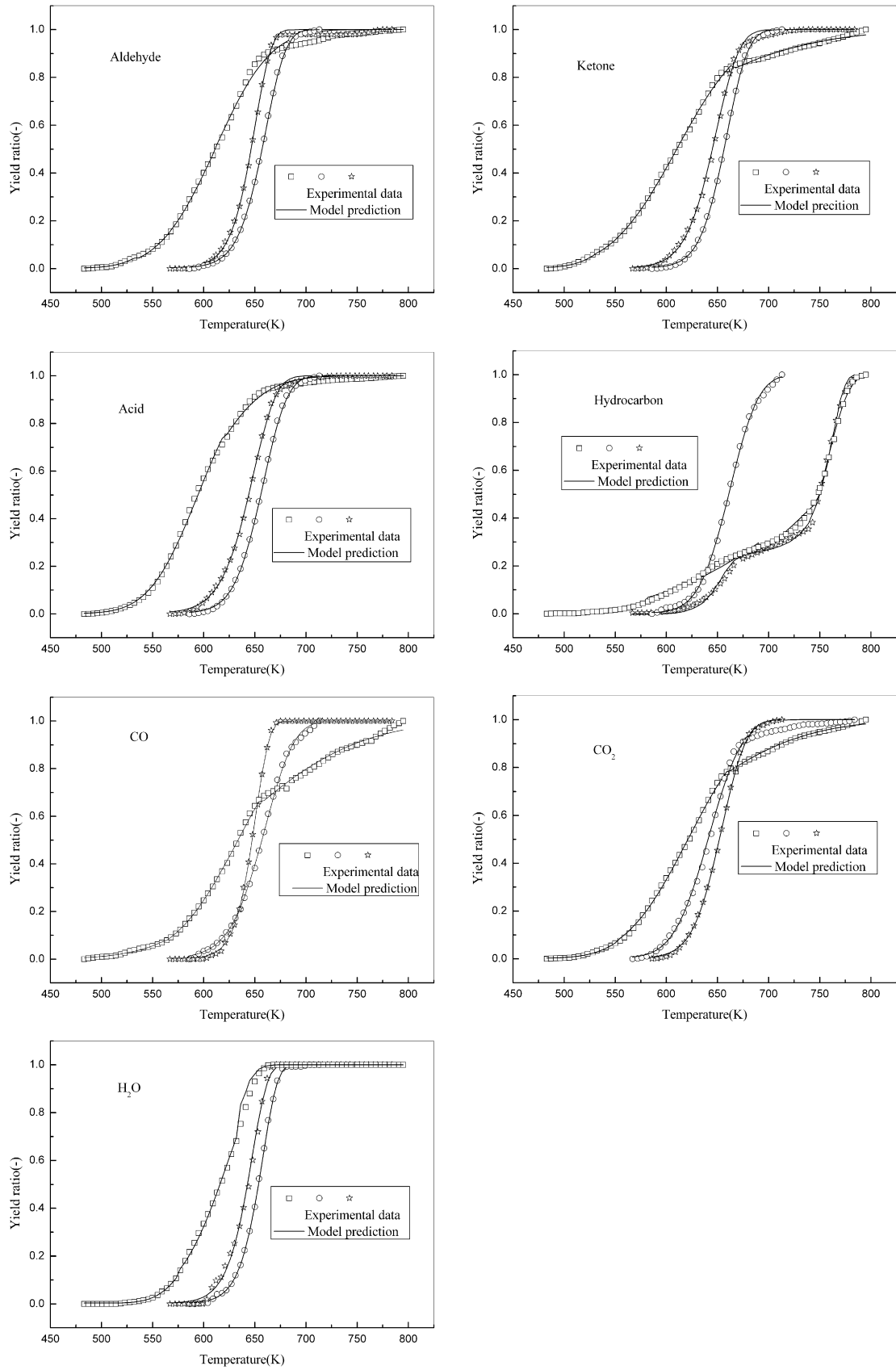
If a given volatile product evolved in multiple peaks, the corresponding pools of the precursor material are numbered 1, 2, etc. Thus, the pyrolysis process of typical medical waste materials can be described completely by many equations. The results of TG-FTIR experiments from ref. [26] were used to fit model parameters to experimental data, and the kinetic parameters are given in Tables 2–4.

Table 3

Kinetic parameters ( $k_0$ ,  $E_0$  and  $\sigma$ ) and correlation coefficients ( $r$ ) for medical respirator pyrolysis

Species	$T$ (K)	$k_0$ ( $\text{s}^{-1}$ )	$E_0$ ( $\text{kJ mol}^{-1}$ )	$\sigma$ ( $\text{kJ mol}^{-1}$ )	$s$	$r$
CO	567–784	$1\text{e}+24$	294.5	1.9	0.000587	0.991
CO <sub>2</sub>	567–784	$1\text{e}+21$	256.0	8.8	0.011694	0.965
H <sub>2</sub> O	567–784	$1\text{e}+19$	232.0	0.5	0.004079	0.990
Hydrocarbon-1	567–675	$1\text{e}+22$	293.5	15.85	0.002417	
Hydrocarbon-2	675–739	$1\text{e}+14$	218.5	48.6	0.001445	0.960
Hydrocarbon-3	739–784	$1\text{e}+17$	243.5	0.5	0.005246	
Aldehyde	567–784	$1\text{e}+20$	245.5	1.8	0.004658	0.973
Ketone	567–784	$1\text{e}+17$	209.0	3.6	0.003594	0.992
Acid	567–784	$1\text{e}+15$	184.5	2.4	0.002215	0.999

If a given volatile product evolves in multiple peaks, the corresponding pools of the precursor material are numbered 1, 2, etc.



**Fig. 2.** Comparison of yield ratio for each pyrolysis product from TG-FTIR experiment and DAEM model prediction (bamboo stick (□), absorbent cotton (○), medical respirator (☆)).

**Table 4**  
Kinetic parameters ( $k_0$ ,  $E_0$  and  $\sigma$ ) and correlation coefficients ( $r$ ) for bamboo stick pyrolysis

Species	$T$ (K)	$k_0$ ( $s^{-1}$ )	$E_0$ (kJ mol $^{-1}$ )	$\sigma$ (kJ mol $^{-1}$ )	$s$	$r$
CO-1	483–559	1e+15	190.5	19.6	0.000142	
CO-2	559–659	1e+16	194.0	14.05	0.000652	0.994
CO-3	659–795	1e+25	292.5	48.45	0.004527	
CO $_2$ -1	483–550	1e+25	293.0	20.5	0.000056	
CO $_2$ -2	550–663	1e+25	295.0	22.5	0.001052	0.996
CO $_2$ -3	663–795	1e+25	276.0	49.0	0.000614	
H $_2$ O-1	483–573	1e+25	291.0	14.15	0.000038	
H $_2$ O-2	573–636	1e+09	108.0	2.2	0.001021	0.988
H $_2$ O-3	636–795	1e+14	166.5	1.55	0.000067	
Hydrocarbon-1	483–627	1e+19	255.5	26.05	0.000179	
Hydrocarbon-2	627–699	1e+07	110.5	21.45	0.000769	0.995
Hydrocarbon-3	699–749	1e+19	274.0	32.2	0.002071	
Hydrocarbon-4	749–795	1e+15	215.5	0.5	0.000959	
Aldehyde-1	483–537	1e+26	295.5	18.5	0.000063	
Aldehyde-2	537–663	1e+09	107.5	4.9	0.001847	0.999
Aldehyde-3	663–795	1e+24	239.5	49.05	0.000148	
Ketone-1	483–537	1e+26	292.0	18.85	0.000086	0.997
Ketone-2	537–668	1e+18	209.5	16.9	0.001210	
Ketone-3	668–795	1e+20	206.0	49.0	0.001637	
Acid-1	483–618	1e+25	282.0	17.0	0.001795	0.987
Acid-2	618–795	1e+10	114.5	8.0	0.003345	

If a given volatile product evolves in multiple peaks, the corresponding pools of the precursor material are numbered 1, 2, etc.

For all these three samples, there are seven kinds of volatile species listed in Tables 2–4. For the absorbent cotton sample, each volatile product evolved in a single peak, this corresponds to 7 equations which describe the pyrolysis of absorbent cotton. For the medical respirator sample, the hydrocarbon product was found to evolve in three peaks, this corresponds to 9 equations which describe the pyrolysis of medical respirator. For the bamboo stick sample, one volatile species evolved as two peaks, five as three peaks, and hydrocarbon as four peaks. The number of equations describing bamboo stick pyrolysis is 21. Each of these expressions had the form of Eq. (7).

Data of Tables 2–4 show that the mean activation energies and pre-exponential factors for the three samples had some differences, this was not surprising as the TG–FTIR data show they had different TG and DTG decomposition peaks. In the same sample, the kinetic parameters were different to each volatile species, since the precursor pool (peak) and pool size to each species were different. This wide range of kinetic parameter was similar to those reported in the literature [12] ( $E_0 = 151–295$  kJ mol $^{-1}$  for CO, CO $_2$ , H $_2$ O, etc.).

The experimental data and model prediction of evolved species are shown in Fig. 2. By comparing the model predictions with the experimental data, the following observations can be made on the basis of Fig. 2:

- The model prediction matched well with the experimental data for all samples.
- The agreement of model prediction and experimental data was excellent for the absorbent cotton, partly because of the fact that all volatile species evolved in a single peak.
- The agreement of model prediction and experimental data was not so accurate for the bamboo stick, compared to the absorbent cotton and the medical respirator. This was partly because the volatile species evolves in multiple peaks, and the thermal decomposition temperature range of the bamboo stick was widest of these three samples.
- The model for hydrocarbon evolution was most complicated of all species because of the fact that the hydrocarbon evolved in the most peaks.

## 5. Conclusions

TG combining with FTIR is a useful tool in dynamic analysis as it monitors continuously the time dependent evolution of the volatile species. Also, kinetic parameters for a pyrolysis model based on parallel, independent, first-order reactions with Gaussian distribution of activated energies were determined from TG–FTIR data of sample and through a direct search method based on the grid technique presented in this study. Determined kinetic parameters can be used to get the yield and rate of evolution for individual pyrolysis products.

The results presented in this work indicated that the model can predict the experimental data with a reasonable accuracy. The present pyrolysis model may be used for stand-alone devolatilization applications as well as for a submodel in a CFD code. Further work should be conducted for other medical waste materials, so that the medical pyrolysis process can be fully understood. The kinetic parameters and pyrolysis model can be used as source terms in the species transport equation in CFD simulation to fulfill the CFD modeling of medical waste pyrolysis. Such a model would be valuable for understanding and improving the medical waste incineration process.

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