Chemical Synthesis Residual Pyrolysis and Combustion: Kinetics and Evolved Gases Investigated by TG-FTIR

FANG Chunqi[1], JIANG Xuguang[1,*], LV Guojun[1], YAN Jianhua[1], LIN Xuliang[2], SONG Huibo[2], CAO Junjun[2]

1. State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China
2. Research and Development Department, Hisun Pharmaceutical Co. Ltd., Taizhou 318000, China

Abstract: Chemical synthetic residual is one of the solid wastes generated from pharmaceutical industry. The pyrolysis and combustion characteristics of chemical synthesis residual were investigated using a thermogravimetric analyser coupled with Fourier transform infrared spectroscopy (TG-FTIR) in this study. The processes of pyrolysis and combustion can be divided into three stages. The average weight loss rate of pyrolysis process at low temperature was higher than that of combustion. The kinetic parameters of chemical synthesis residual during pyrolysis and combustion were calculated based on the TG results. Acetic acid and 4-aminophenol were the main evolved matter observed in the pyrolysis process. The emission characteristics of combustion at low temperature were similar to that of the pyrolysis, while CO_2 was found as the major gaseous product at high temperature. A high temperature about 850°C is needed to make sure the complete combustion of chemical synthesis residual.

1. Introduction

Chemical synthesis pharmaceutical is the process of producing active components of drugs by a series of chemical reactions. It involves a complex combination of mechanical and chemical processes which are mainly divided into three fundamental sub-processes [1]. First, pharmaceutical intermediates are synthesized by chemical materials. Next, the drug structure is modified to obtain the target product. The final product is obtained by the finishing operations which may include removing the protection basis, extracting, refining and drying. The process flow and sewage nodes are shown in Fig. 1. The series of operations involved in pharmaceutical generate substantial quantities of solid, liquid, and gaseous wastes. Chemical synthetic residual is classified as hazardous waste (HW02 toxicity) because of their threats to human health and the environment [2]. Pharmaceutical manufacturing wastes are piled up in the fixed place in the factory and sent to the qualified unit for processing regularly. However, with the rapid development of the enterprise, problems such as insufficient stacking site capacity, deteriorating environmental conditions in the factory area, and higher costs of waste pharmaceutical residue treatment have become prominent. The disposal of a large amount of chemical synthesis residual generated in the pharmaceutical industry has become a problem to be solved.
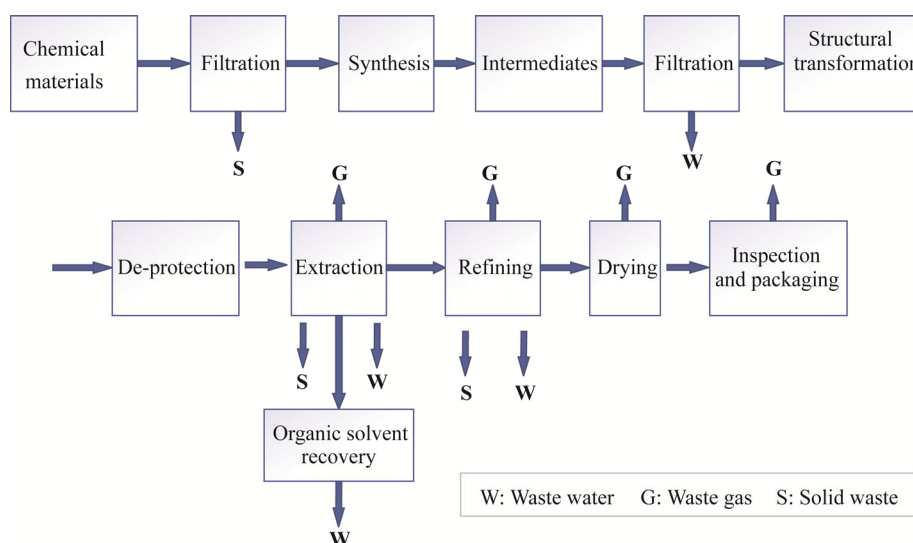
Fig. 1   Chemical synthesis pharmaceutical process flow and sewage nodes

Incineration is a common technique to treat waste to reduce waste mass and recycle energy [3], while incineration also results in bottom ashes, fly ashes and gaseous pollutants [4,5]. In addition, pyrolysis is the thermal destruction of organic materials in the absence of oxygen. Some liquid fuels, gases and carbon can be obtained during pyrolysis [6,7]. Pyrolysis is the preferred method for treating organic wastes in some cases. The study of Jiang et al. [8] showed that dyestuff residue started decomposing below 200°C when heated in an inert atmosphere, and SO_2, HCN, CO_2 and CH_3OH were detected as the main pyrolysis products. Du et al. [9] presented an investigation on the cofiring characteristics of bio-ferment with coals, and found ignition temperature basically decreased with increasing bio-ferment cofiring ratio as well as combustion rate. The thermal behaviors of chemical synthesis residual are still unclear, and thermal decomposition can also be affected by many factors. Therefore, it is necessary to understand the evolution characteristics of chemical synthetic residue during pyrolysis and combustion.

Thermogravimetric analysis (TGA) is generally used to investigated the decomposition of wastes under both nitrogen and air atmospheres, and the differential thermogravimetric (DTG) curves and kinetic parameters can be obtained from TGA results [10,11]. On the other hand, the evolution of gaseous products during TG experiments can be investigated by Fourier transform infrared spectroscopy (FTIR) [12]. In this paper, the thermal behaviors chemical synthesis residual during pyrolysis and combustion are studied by TG-FTIR analysis, and the results of weight loss, kinetic parameters and the evolution of gaseous products provided abundant information for understanding pyrolysis and combustion characteristics of chemical synthesis residual.

2. Experiments

2.1 Material

The chemical synthesis residual used in this study is originated from the synthesis of antipyretic analgesic drug-acetaminophen ($C_8H_9NO_2$). The chemical composition of the residual produced by the process is usually easy to master due to the characteristics of the chemical synthesis process. The main components of the residual are acetaminophen, aminophenol, acetic acid, water and sodium sulfate. The results of proximate and ultimate analysis of the sample were listed in Table 1. Prior to the experiment, the samples were dried in an oven for three hours at 105°C, then the samples were crushed and pulverized to a size of <0.2 mm. Approximately 10 mg sample was used in both combustion and pyrolysis.

Table 1   Ultimate and proximate analysis of the chemical synthesis residual

| Property	Concentration/wt.%
Ultimate analysis	
C	62.52
H	4.60
O	14.57
N	7.62
S	0.38
Proximate analysis	
Moisture	7.63
Ash	2.68
Volatiles	83.64
Fixed carbon	6.05
High heating value/MJ·kg^{-1}	25.51

2.2 Method

The TG-FTIR system consists of a thermo analyzer (TGA/SDTA851^e, Mettler Toledo, Switzerland) and a fourier infrared spectrometer (Nexus-670, Nicolet, USA), which can continuously detect the evolving products. The stainless-steel transfer tubes and gas cell (20 cm optical path length) were heated to 180°C to minimize secondary reactions. Nitrogen was used as a carrier gas due to its inertia, and the flow rate during pyrolysis was 20 ml·min^{-1}; air was used as an oxidant during combustion at the same flow rate. The heating rate was 30°C·min^{-1} and the final temperature was 950°C. Other specifications for this research included the following: the resolution in FTIR was set as 4 cm^{-1}; the spectrum scan frequency was set to 20 times·min^{-1}; and the spectral region was set as 4000–400 cm^{-1}.

3. Result and Discussion

3.1 TG data analysis

During pyrolysis and combustion, the TG/DTG profiles of chemical synthesis residual are shown in Fig. 2 at the heating rate of 30°C·min^{-1}. According to DTG profile, pyrolysis can be divided into three stages. The weight loss of the first stage was mainly caused by sample drying (T < 200°C), water and volatile substances are released in this stage. The second stage was rapid thermal decomposition of chemical synthesis residual between 200°C and 395°C. Most of the weight loss (about 74.34% of the total weight) occurred at this stage. The weight loss rate peaked at 335°C (38.00%·min^{-1}). The final stage was further cracking in the temperature range from 395°C to 950°C. At this stage, only about 5.13% of the weight was lost at a low rate. The results showed that the pyrolysis of chemical synthesis residual was basically completed around 400°C. When the temperature reached 950°C, the total weight decreased by 85.43%.
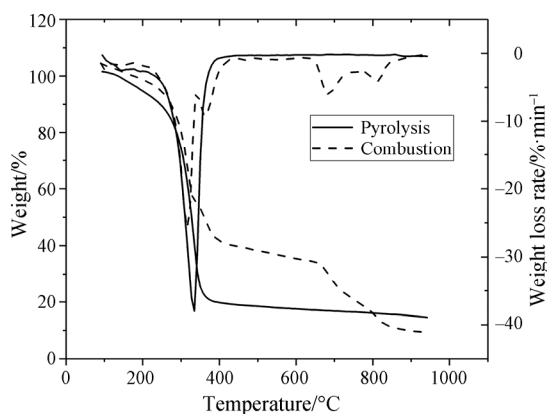
Fig. 2 TG/DTG profiles for the pyrolysis and combustion of chemical synthesis residual

Exactly as pyrolysis, the combustion process can also be divided into three stages (100°C–200°C, 200°C–420°C, 420°C–950°C). The first stage, with the release of water and volatile substances from the sample, was similar to the stage under nitrogen. The second stage was mainly the emission of volatile components from chemical synthetic residual, and the maximum value of the DTG curve was reached at 315°C. For some organic wastes [13,14], the DTG curves of pyrolysis and combustion matched together except in the last part. However, it was found that the weight loss rate in the second stage was less than that of the pyrolysis in this study. Maybe the oxidation of some components that could have been decomposed or evaporated in N$_2$ atmosphere led to a lower weight loss rate. There was a great difference between combustion and pyrolysis in the third stage. The combustion of the residue mainly occurred from 644°C to 855°C, and about 23.38wt.% of the sample lost in this temperature range. It was shown that 850°C was enough for complete combustion of chemical synthesis residual, and a total weight loss of 90.60% was discovered.

3.2 Kinetic parameters of chemical synthesis residual during pyrolysis and combustion

The kinetic parameters of chemical synthesis residual during pyrolysis and combustion can be calculated based on the results of TG experiment [13,15,16].

In TG analysis, the mass loss fraction is defined as:

$$\alpha = (M_1 - M_2)/(M_1 - M_3) \qquad (1)$$

where M$_1$ is initial mass; M$_2$ is the mass during thermal degradation process; M$_3$ is the final mass when experiment finished.

The rate constants in dynamical equations are closely related to temperature. And the most commonly used relation was proposed by Arrhenius. Under non-isothermal conditions, the activation energy E conforms the equation (2):

$$\frac{d\alpha}{dT} = A/\beta \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (2)$$

where R is universal gas constant (R=8.314 J·mol·K^{-1}); β is heating rate; A is pre-exponential factor; T is reaction temperature; E is activation energy; and $f(\alpha)$ is the differential form of kinetic mechanism function.

Thermal dynamic computation has many methods. The equation was solved using the TG experimental data following the Coats–Redfern method in this work [17,18]:

If $n \neq 1$,

$$\ln\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (3)$$

If n=1,

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (4)$$

where, n is the order of reaction.

For most reaction, $E/RT \geq 1$, and $1-2RT/E \approx 1$. Thus, based on Eq. (3), the plot of the left side of the equation versus $1/T$ can fit to a straight line. The maximum of R^2 can be obtained by adjusting n. The value of A and E can therefore be obtained according to the intercept and slope of the line.

The reaction stages of combustion and pyrolysis can be divided according to the peaks of DTG curves. The process of combustion was subdivided into three steps (Combustion I, II, III), while only one step for the pyrolysis process. The kinetic parameters for each step during chemical synthesis residual pyrolysis and combustion were given in Table 2. It was observed that the activation energy in Combustion I was larger than that of Pyrolysis I, and the activation energy in Combustion II or Combustion III for residue combustion was much larger than Combustion I for the decomposition of sample. It was included that the thermal decomposition

of chemical synthesis residual could be slowed down by oxygen atmosphere in low temperature.

3.3 Infrared spectrum analysis of gaseous products

The spectrum for pyrolysis products of the sample at 195°C was shown in Fig. 3, and only acetic acid was found as the pyrolysis product. It was indicated that acetic acid was evaporated from the sample due to its low boiling point. The spectrums of pyrolysis products at 335°C and 500°C were shown in Fig. 4. Major compounds released at 335°C were identified as acetic acid and 4-Aminophenol, which was caused by the decomposition of acetaminophen, as shown in Eqs. (5). It was found that the absorbance of 4-Aminophenol or acetic acid at 500°C were much lower than that at 335°C, which indicated that the decomposition of acetaminophen almost finished around 500°C.

$$C_8H_9NO_2 + H_2O \rightarrow C_6H_7NO + CH_3COOH \qquad (5)$$
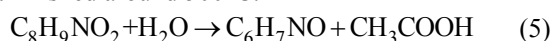
Table 2   Kinetic parameters of chemical synthesis residual during pyrolysis and combustion

Series	Temperature range/°C	Activation energy/kJ·mol⁻¹	pre-exponential factor	R^2	n
Pyrolysis I	200–390	65.62	2.12×10^5	0.9950	0.3
Combustion I	200–390	74.71	2.02×10^6	0.9931	0.9
Combustion II	630–765	621.95	1.14×10^{34}	0.9952	3.4
Combustion III	770–860	586.30	4.15×10^{28}	0.9996	2
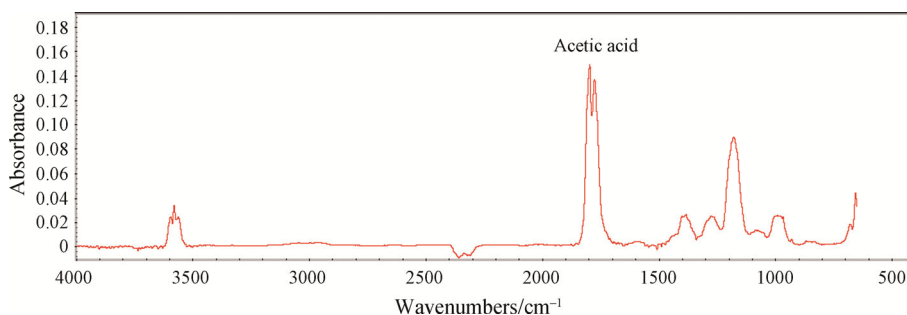
Fig. 3   FTIR spectrum for pyrolysis products evolving from chemical synthesis residual sample, at 195°C
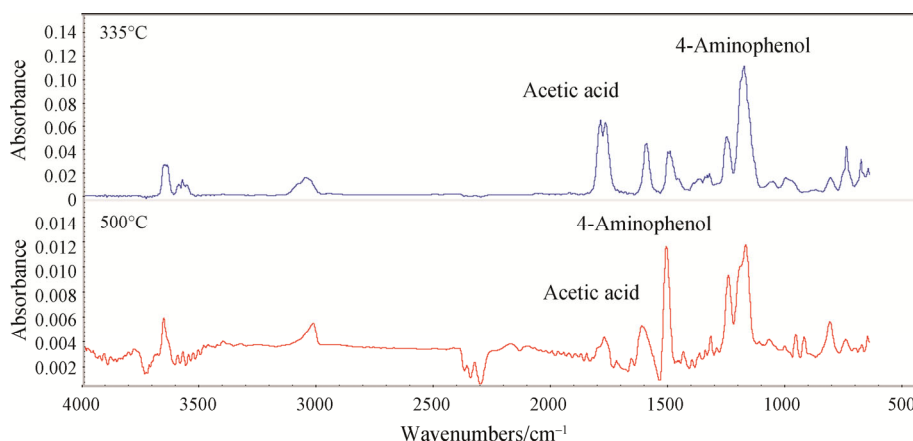

Fig. 4   FTIR spectrum for pyrolysis products evolving from chemical synthesis residual sample, at 335°C and 500°C
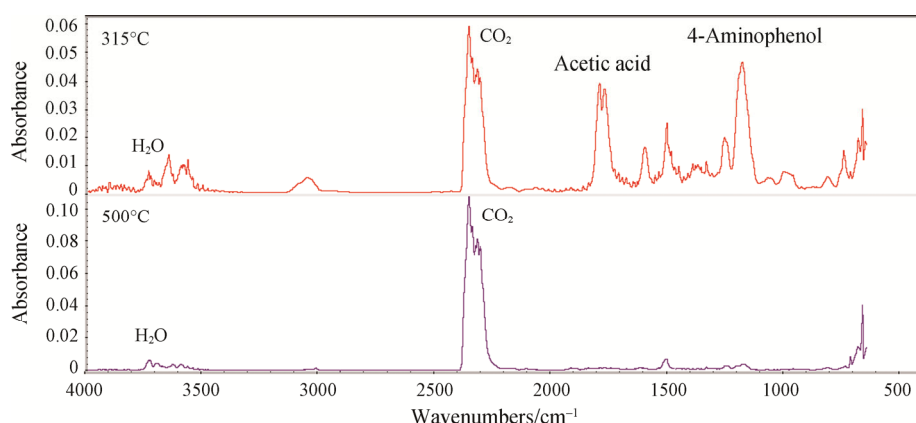
Fig. 5 FTIR spectrum for combustion products evolving from chemical synthesis residual sample, at 315°C and 500°C

The emission characteristics in chemical synthesis residual combustion were also analyzed for comparison with pyrolysis, as shown in Fig. 5. The main gaseous products at 315°C were CO_2, acetic acid, 4-Aminophenol and H_2O. Only a part of acetic acid and 4-Aminopheno were oxidized to CO_2, which showed that the oxidation ability of oxygen was poor at low temperature. A great difference of the emission characteristics between combustion and pyrolysis was found according to the FTIR spectrum for combustion products at 500°C. CO_2 and H_2O were identified as the main combustion gaseous products, caused by the oxidation of acetic acid and 4-Aminopheno, as shown in Eqs. (6) and (7).

$$C_6H_7NO + O_2 \rightarrow CO_2 + H_2O + NO_x \qquad (6)$$

$$CH_3COOH + O_2 \rightarrow CO_2 + H_2O \qquad (7)$$
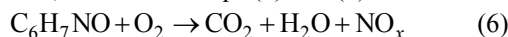
The absorption intensities of acetic acid and 4-Aminophenol in the pyrolysis process varied with temperature, as shown in Fig. 6. Acetic acid was mainly emitted from 93°C to 396°C; the release process could be divided into two stages (93°C–300°C, 300°C–396°C). The first stage represented the evaporation of the acetic acid. The second stage was in the temperature range of 300°C–396°C, owing to the decomposition of acetaminophen. Most of 4-Aminophenol was emitted at 313°C–396°C, which coincided with the release of acetic acid in the second stage. It was indicated that acetic acid and 4-Aminophenol had the same source, acetaminophen.

The evolution of absorption intensity of gaseous products with temperature during chemical synthesis residual combustion were also investigated, as shown in Fig. 7. The emission characteristics of acetic acid and 4-aminophenol in low temperature combustion were similar to those of pyrolysis, which also confirmed that oxidation ability of oxygen was poor at low temperature. Besides, small peaks of acetic acid and 4-Aminophenol were also observed at 700°C during combustion, which caused by the further decomposition of residual. Acetic acid and 4-Aminophenol were not completely oxidized to
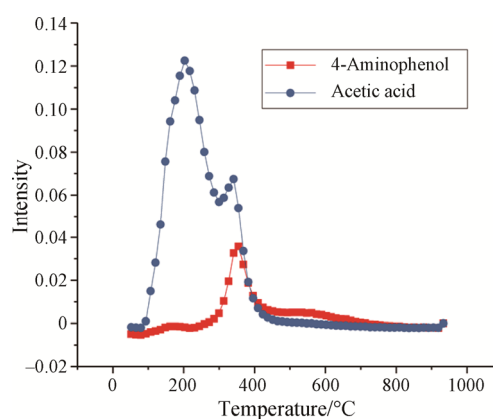
Fig. 6 Evolution of gaseous products with temperature during pyrolysis
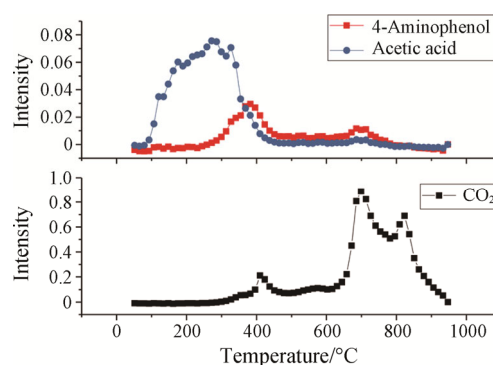
Fig. 7 Evolution of gaseous products with temperature during combustion

CO_2 and H_2O due to the short residence time for combustion. Most of CO_2 was emitted at 630–892°C, and the maximum emission of CO_2 occurred around 700°C and decreased quickly after the secondary peak around 823°C. It is indicated that a high temperature about 850°C is necessary for the complete combustion of chemical synthesis residual. Although nitrogen-containing gaseous products were not detected in this

study, the emission of nitrogen containing pollutants still needs to be paid attention considering the high content of nitrogen in the chemical synthesis residual.

4. Conclusion

In this study, the characteristics of chemical synthesis residual pyrolysis and combustion were investigated by the TG-FTIR analysis. The TG and DTG curves of pyrolysis and combustion could both be divided into three stages. It was found that the weight loss rate of the combustion in the second stage was less than that of the pyrolysis, not like some organic wastes. It was found that the decomposition of chemical synthesis residual can be slowed down under oxygen atmosphere at low temperature by comparing the kinetic parameters of pyrolysis and combustion.

Only acetic acid and 4-aminophenol were found as main gaseous products during pyrolysis through infrared analysis, and they were mainly emitted in a temperature range from 100°C to 400°C. The pyrolysis of chemical synthesis residual almost finished after 400°C. The emission characteristics of combustion at low temperature were similar to that of the pyrolysis process, while CO_2 was found as the dominant gaseous product at high temperature. It was found that oxygen had a poor oxidizing ability at low temperature in chemical synthesis residual combustion, so a high temperature about 850°C was needed to make sure the complete combustion of chemical synthesis residual. Furthermore, the emission of nitrogen-containing gases during combustion should be focused on due to the high content of nitrogen in the chemical synthesis residual.

Acknowledgments

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