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The study of thermal decomposition of 2-bromo-3,3, 3-trifluoropropene and its fire-extinguishing mechanism



Xiaomeng Zhou^{a,*}, Weiwang Chen^a, Mingyong Chao^b, Guangxuan Liao^c

^a The College of Environmental Science and Engineering, Nankai University, Tianjin 300071, PR China

^b Department of Chemistry and Chemical Engineering, Heze University, Heze, Shandong 274015, PR China

^c State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

As a new kind of Halon replacement, 2-bromo-3,3,3-trifluoropropene (BTP) is highly effective at fire suppression with an extinguishment concentration lower than that of Halon 1301. Although the physical properties and extinguishing characteristics of BTP have been widely reported, there are relatively few studies on its thermal pyrolysis and extinguishing mechanisms. In this study, the thermal decomposition of BTP was studied over a temperature range of 25–800 °C and the decomposition products were analyzed by GC and GC–MS. Experimental results showed that the decomposition products were mainly trifluoropropyne (CF₃CCH) and/or bromotrifluoromethane (CF₃Br). The calculated apparent activation energies for the thermal pyrolysis of BTP by first order reaction approximation were in excellent agreement with the theoretical calculation results by Gaussian 03. Furthermore, by analyzing decomposition products and their chemical inhibition effect, thermal decomposition mechanism of BTP and its chemical extinguishing mechanism at high temperature were then proposed.

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1. Introduction

The Montreal Protocol (1987), along with its subsequent amendments, has mandated a ban on the production and application of Halons and chlorofluorocarbons (CFCs) due to their considerable destruction to stratosphere ozone via BrO_x and ClO_x catalytic cycles [1-5]. For this, tremendous efforts have been made to search for suitable Halons and CFCs replacements over the recent years. Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), such as HFC-227ea and HFC-236fa, have been reported to be clean agents and are being used as substitutes for Halons [6-8]. However, HFCs and HCFCs will eventually be phased out of application in the foreseeable future due to their unacceptably long atmospheric lifetime (ALT) and high global warming potential (GWP) [9]. Thus, it is still an arduous task to find more advanced Halon replacement agents that have superior fire suppression performance and acceptable environmental, physical and toxicological properties [10-12].

2-Bromo-3,3,3-trifluoropropene ($CF_3CBr = CH_2$, BTP) has been selected as one kind of Halon replacements as the molecule contains both bromine atom for chemical fire-suppression activity and a carbon–carbon double bond to promote tropospheric

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degradation, which should result in a short atmospheric lifetime. The average cup burner extinguishment concentration of BTP (2.6% by volume) is considerably lower than that of Halon 1301 [13]. According to K.O. Patten, BTP is among the shortest-lived of bromocarbons evaluated thus far, with a lifetime of 4.3–7.0 days. As a result, the potential effects of BTP on ozone and climate are only 0.0028-0.0052 and 0.0028-0.0050 for ODP and GWP (100year time horizon) respectively [14]. Furthermore, due to its relatively low boiling point (34–35 °C at atmospheric pressure) and high vapor pressure (0.74 bar at 25 °C), BTP can be readily gasified to reach its extinguishment concentration in a confined space. BTP is also a substance of low toxicity with the NOAEL and LOAEL values of 0.5% and 1.0% (vol.%) respectively, as low as the toxicity testing data of Halon 1211 [11]. Thereby, BTP would be an excellent Halon replacement agent from the point view of its acceptable environmental, physical and toxicological properties.

The physical properties and extinguishing characteristics of BTP have been widely reported in recent years, however, very few researches have been conducted on the thermal pyrolysis of BTP and its fire-extinguishing mechanism. For example, Orkin [14,15] studied a possible degradation mechanism of bromoalkenes in atmosphere using the flash photolysis resonance fluorescence technique. In addition, HF production mechanism of BTP in fire extinguishing process was calculated previously at B3LYP/6-311++G(d,p) theory level by our research group[16]. Zhang and Lin [17] investigated the decomposition of 1-bromo-3,3,3-trifluoropropene by Gaussian 98



^{*} Corresponding author. Tel.: +86 22 23504894; fax: +86 22 23507765. *E-mail address*: zhouxm@nankai.edu.cn (X. Zhou).

and pointed out three possible decomposition pathways for 2bromo-3,3,3-trifluoropropene. By evaluating the suppressing performance of water mist with bromofluoropropene on gasoline pool fires, Ni and Chow [18] also approached the physical and chemical inhibition effect of BTP briefly. However, most of these reported researches focused mainly on the theoretical level, lacking experimental validation. Therefore, further experimental researches are necessary to illustrate the pyrolysis of BTP and its fire-extinguishing mechanism.

In this study, BTP was pyrolyzed with a flow of nitrogen carrier gas in a tubular pyrolysis reactor over the temperature range of 25–800 °C. Its decomposition products were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). Then, the apparent activation energy for the thermal pyrolysis of BTP was calculated by first order reaction approximation based on experimental data, and the bond dissociation energies (BDEs) and energy barriers were calculated by Gaussian 03 at the B3LYP/6-311++G(d,p) theory level. Finally, combined with theoretical calculation results, decomposition and extinguishing mechanisms of BTP were emphatically studied by analyzing decomposition products and their chemical inhibition effect. This research may provide guidance to the optimal design of BTP-based fire suppression system and facilitate the industrial application of BTP.

2. Results and discussion

2.1. Experimental results

Pyrolysis of BTP was studied in a tubular pyrolysis reactor at a constant heating rate of 3 °C min⁻¹ from 25 °C to 800 °C. Fig. 1 shows the decomposition ratios of BTP at various temperatures in carrier gas of nitrogen with a fixed mole fraction of BTP (20%) and a constant nitrogen flow rate of 5.5 mL s⁻¹. From the figure we can see that BTP exhibits great stability and extremely low decomposition ratios when the temperature is below 600 °C, which indicates that at a temperature lower than 600 °C, it is the BTP molecules rather than decomposition products react with reactive radicals within the flame to stop the combustion reaction [19]. When the temperature rises above 600 °C, there is a rapid increase in the decomposition ratio of BTP. Besides, during the course of the experiment, obvious carbonization of BTP was observed above 760 °C.

Based on the decomposition curve of BTP as illustrated in Fig. 1, pyrolytic behavior of BTP was further studied in a carrier gas of nitrogen at various temperatures in a range from 600 °C to 800 °C.



Fig. 1. The decomposition ratios of BTP at various temperatures with a flow of nitrogen carrier gas.



Fig. 2. The decomposition ratios of BTP at various temperatures with three different residence time of 3 s, 5 s, 10 s.

Fig. 2 shows the decomposition ratios of BTP in a carrier gas of nitrogen with three different residence time of 3 s, 5 s and 10 s at various temperatures. From the curves in the figure we can see that the decomposition ratio of BTP is a monotonically increasing function of temperature and higher temperature corresponds to higher decomposition ratio of BTP. Besides, a longer residence time in the reactor also results in a higher decomposition ratio. Fig. 3 shows the decomposition ratios of BTP in a carrier gas of nitrogen with three different initial mole fractions (10%, 20% and 50%). From the figure we can see that the decomposition ratio of BTP increases rapidly with the increase of pyrolysis temperature, while no obvious influence by the initial mole fraction of BTP was observed.

2.2. Chemical kinetics analysis

From the perspective of chemical kinetics, if the reaction rate of the thermal decomposition is assumed to be proportional to the first order of BTP concentration, the following equation can be used:

$$\ln\left[\frac{A(\text{BTP})}{A_0(\text{BTP})}\right] = \ln(1-\alpha) = -k(\text{BTP})t \tag{1}$$

where α (%) = 1 – *A*(BTP)/*A*₀(BTP) is the decomposition ratio of BTP, *t* (s) is the reaction time, and *k*(BTP) is the first-order rate



Fig. 3. The decomposition ratios of BTP at various temperatures with three different initial mole fraction of 10%, 20% and 50%.

coefficient for the BTP pyrolysis, expressed by the Arrhenius equation as follows:

$$k = A \exp\left(\frac{E_a}{RT}\right) \tag{2}$$

where $E_a(kJ \text{ mol}^{-1})$ is the activation energy, $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ is the ideal gas constant, A is the pre-exponential factor and T(K) is the absolute temperature.

Eq. (3) was obtained by introducing Eq. (2) into Eq. (1). Note that, for first order chemical reaction, the thermal decomposition ratio is irrelevant to the initial concentration of the reactant. And in a narrow temperature range, there must be a linear correlation between $\ln \ln[1/(1 - \alpha)]$ and 1/T with a fixed residence time (see Eq. (4)).

$$\ln(1-\alpha) = -A \exp\left(\frac{-E_a}{RT}\right)t$$
(3)

$$\ln \ln \left[\frac{1}{1-\alpha}\right] = -\frac{E_a}{RT} + \text{constant}$$
(4)

Based on the experimental data of the three different initial mole fraction experiments with a fixed residence time of 5 s, the calculation results of Eq. (4) are plotted in Fig. 4. From the plot it can be observed that the relationship between $\ln \ln[1/(1 - \alpha)]$ and 1000/T is linear, and fitted well. So, it is reasonable to assume the thermal degradation of BTP to be the first order reaction from above calculation and Fig. 3. The apparent activation energies calculated are $314.2 \text{ kJ} \text{ mol}^{-1}$, $328.4 \text{ kJ} \text{ mol}^{-1}$, $310.7 \text{ kJ} \text{ mol}^{-1}$ with the relative error within 6% and the results are categorized in Table 1.

2.3. Theoretical analysis by Gaussian 03

In order to reveal the thermal decomposition of BTP and its fire extinguishing mechanisms, theoretical analysis by Gaussian 03 was performed. Density function theory (DFT) method accompanied with 6-311++G(d,p) basis set was employed to do this. During the calculation, geometrical optimization and frequency analysis for BTP, including feasible decomposition products or fragments, and transition states, were probed theoretically with Gaussian 03 at the B3LYP/6-311++G(d,p) theory level. Besides, connections between reactants, transition structures and products were confirmed by intrinsic reaction coordinate (IRC) calculation. Part of the calculation results, such as molecular structure of BTP and corresponding optimized geometrical parameters, are depicted in



Fig. 4. Relationship between $\ln \ln [1/(1 - \alpha)]$ and 1000/T.

Table 1

The fitted equations and thermodynamic data calculated in Fig.5.

Mole fraction	Fitted equation	<i>R</i> ²	Apparent E _a (kJ mol ⁻¹)
10%	$\ln \ln[1/(1-\alpha)] = 36.87 - 37.37 \times 10^3/T$	0.9551	310.7
20%	$\ln \ln[1/(1-\alpha)] = 39.36 - 39.50 \times 10^3/T$	0.9850	328.4
50%	$\ln \ln[1/(1-\alpha)] = 37.52 - 37.79 \times 10^3/T$	0.9908	314.2

Fig. 5. The same goes for the possible transition states. Beyond that, the bond distances and bond dissociation energies (BDEs) for BTP molecular associated with energy barriers for three feasible decomposition pathways, which were listed in Table 2, were also investigated at the same basis set and theory level. All BDEs and energy barriers involved in the dissociation and decomposition reactions of BTP are expressed by thermal enthalpies that corrected by zero point energy, based upon frequency calculation (freq = temperature = 873.15) by Gaussian 03.

From the theoretical calculation results we can see that the dissociation energy of C-Br bond (308.2 kJ mol⁻¹) is the lowest among all the bonds in the BTP molecule. The long bond distance and low dissociation energy mean that the bond is loosely attached and easy to break, and Brº radical can be easily formed at a relatively lower energy. Besides, bond dissociation energy of C-C bond (386.3 kJ mol⁻¹) is much lower than BDE values of C-F, C-H and C=C bonds except for C-Br bond. The conclusion draw from above is that BTP molecule may provide CF₃[•] and Br[•] radicals at high temperature, which are very effective in extinguishing a fire. In addition, the energy barriers of three possible decomposition pathways were also calculated using TS method, among which the pathway 1, CF₃CBrCH₂-TS₁-CF₃CCH + HBr, was calculated to have the lowest energy barrier of 300.1 kJ mol $^{-1}$. Another pathway that leads to product channel, CF₂ + FBrCH₂, has an energy barrier of 437.1 kJ mol⁻¹. The calculation results indicate that the most probable dissociation products should be (CF₃CCH + HBr) for the lowest energy barrier. Likewise, $(CF_3Br + CCH_2)$ with energy barrier of 502.0 kJ mol⁻¹ should be the most difficult products to produce.

$$CF_{3}CBr = CH_{2} \begin{cases} \frac{300.1 \text{ kJ} \text{ mol}^{-1}}{TS_{1}} CF_{3}CCH + HBr \\ \frac{437.1 \text{ kJ} \text{ mol}^{-1}}{TS_{2}} CH_{2}CFBr + CF_{2} \\ \frac{502.0 \text{ kJ} \text{ mol}^{-1}}{TS_{3}} CF_{3}Br + CCH_{2} \end{cases}$$

To verify the above theoretical calculation results and investigate the decomposition products of BTP, the gaseous products were also detected by GC–MS. Analysis of the obtained mass spectrum reveals two major decomposition products. One with the characteristic fragments at m/z = 69, 75 and 94 (molecular ion

able 2	
DEs and energy barriers calculated by Gaussian 03.	

Bonds/ pathways	Bond distance (Å)	Reaction equations	BDEs/energy barriers (kJ mol ⁻¹)
C–Br	1.906	$CF_3CBrCH_2-CF_3(C^{\bullet})CH_2+Br$	308.2 ^a
C–C	1.511	$CF_3CBrCH_2-CF_3^{\bullet}+CH_2(C^{\bullet})Br$	386.3 ^a
C=C	1.325	$CF_3CBrCH_2-CF_3(C^{\bullet})Br+CH_2^{\bullet}$	727.9 ^a
(C-F) ₁	1.350	$CF_3CBrCH_2-CH_2CBrCF_2^{\bullet}+F^{\bullet}$	447.7 ^a
$(C-F)_2$	1.348	CF ₃ CBrCH ₂ -CH ₂ CBrCF ₂ •+F•	479.8 ^a
(C-H) ₁	1.083	$CF_3CBrCH_2-CF_3CBrCH^{\bullet}+H^{\bullet}$	464.9 ^a
$(C-H)_{2}$	1.081	$CF_3CBrCH_2-CF_3CBrCH^{\bullet}+H^{\bullet}$	471.5 ^a
Pathway 1	_	CF ₃ CBrCH ₂ -TS ₁ -CF ₃ CCH + HBr	300.1 ^b
Pathway 2	_	CF ₃ CBrCH ₂ -TS ₂ -CF ₂ •+CFBrCH ₂	437.1 ^b
Pathway 3	-	$CF_3CBrCH_2-TS_3-CF_3Br+CCH_2$	502.0 ^b

^a Bond dissociation energy (BDE) values of different bonds.

^b Reaction energy barriers of three feasible decomposition pathways for BTP.



Fig. 5. Geometrical optimization of BTP and three possible transition states.

peak) is proved to be CF_3CCH , and the other with molecular ion peak at m/z = 148 is CF₃Br. Nonetheless, the principal product varies with the pyrolysis temperature. In a temperature range of 600–700 °C, CF₃CCH is detected to be the principal product; while when the temperature rises above 700 °C, the major product turned out to be CF₃Br. That is, for BTPs thermal decomposition, the formation of CF₃Br requires more energy than the formation of CF₃CCH. It is worthwhile to note that, however, no clear evidence in mass spectrum can prove the formation of CFBrCH₂ during our whole experiment. This is probably because that the CF₃Br is mainly formed by CF3[•] and Br[•] radicals dissociated from different BTP molecules rather than formed by monomolecular cracking reaction. In this case, CF₃Br can be generated with much less energy. Besides, the apparent activation energies calculated above by first order reaction approximation fall among the energy barrier of reaction path 1 and BDE values of C-Br and C-C bonds, which shows that experimental results and theoretical analysis receive excellent agreement. The high apparent activation energy can also explain the good stability of BTP which requires a pyrolysis temperature of 600 °C.

2.4. Thermal decomposition and extinguish mechanisms

Based on above experimental results and theoretical analysis, the thermal decomposition mechanism of BTP can be summarized as follows. When the temperature reaches to 600 °C, the lowest energy barrier (300.1 kJ mol⁻¹) is overcome and the decomposition of BTP begins, leading to the formation of (CF₃CCH + HBr). As the temperature rises, CF₃• and Br• radicals will be dissociated from different BTP molecules for a little higher energy required, and contribute to the generation of CF₃Br. Almost all decomposition products and radicals, such as CF₃•, Br•, CF₃Br, make significant contribution to extinguishing a fire.

Like Halons, BTP is a chemically acting fire extinguishant. The contribution of chemical mechanism to the extinguishment of fires predominates over the physical mechanism. It is necessary to probe into the chemical effect of these products and radicals on fire extinguishment. In earlier reports on flame inhibition, Rosser and Wise [20] suggested the basic mechanism of flame inhibition by halogen compounds and pointed out that Br[•] radical makes a great contribution to the extinguishment of a fire by removing the propagating radicals in a flame. The inhibition mechanism has been further justified and refined by Butlin and Simmons [21], Westbrook [22,23] etc., and was widely cited in recent years. Takahashi et al. [24] and Hamins [25] suggested that hydrogen atoms and hydroxyl radicals are the main active species in combustion and are converted to relatively unreactive H₂ or H₂O molecules through the following catalytic cycle:

$$HBr + H^{\bullet} \rightarrow H_2 + Br$$

 $HBr\,+\,OH^{\bullet}\rightarrow\,H_2O\,+\,Br$

Besides, Westbrook [22] pointed out that the bromine catalytic cycle reactions are the important pathway in regeneration of HBr, though the direct reaction $H^{\bullet} + Br^{\bullet} + M \rightarrow HBr + M$ has rather slower kinetics.

$$H^{\bullet} + Br^{\bullet} + M \rightarrow HBr + M$$

 $Br^{\bullet} + Br^{\bullet} + M \rightarrow Br_2 + M$

 $H^\bullet \ + \ Br_2 \ \rightarrow \ HBr \ + \ Br^\bullet$

In addition to the above reports, chemical suppression and thermal decomposition of CF_3^{\bullet} and related radicals have been deeply studied previously by other researchers [26–34]. The extinguishing mechanism reactions that promote the consumption of propagating radicals in a flame are summarized in Table 3, which contribute CF_3^{\bullet} to be an efficient fire extinguishing group.

In consideration of the experimental results and the BDEs and energy barriers calculated by Gaussian 03, the reaction fluxes for the decomposition of BTP are summarized in Fig. 6, together with the chemical extinguishing mechanism at high temperature which mostly depending on Br[•], $CF_3^{•}$ and related radicals.

Table 3	
Summary of mechanism reactions that CF ₃ • extinguish a fire.	

No.	Mechanism reactions	References
1	$CF_3Br \longrightarrow CF_3 + Br$	[34]
2	$CF_3 + H \rightarrow CF_3H$	[26,27,29,32]
3	$CF_3H \rightarrow CF_2 + HF$	[32]
4	$CF_3H + H \rightarrow CF_3 + H_2$	[26,28,29,31]
5	$CF_3H + OH \rightarrow CF_3 + H_2O$	[26,28,29–31]
6	$CF_3H \rightarrow CF_2 + HF$	[29,33]
7	$CF_3 + OH \rightarrow CF_2O + HF$	[28,29,33,34]
8	$CF_3 + H \rightarrow CF_2 + HF$	[30,32,33]
9	$CF_3 + O \rightarrow CF_2O + F$	[26,30,32,33]
10	$CF_3 + F \rightarrow CF_4$	[30,34]
11	$CF_4 + H \rightarrow CF_3 + HF$	[30]
12	$CF_2 + O \rightarrow CO + 2F$	[30,32]
13	$CF_2 + OH \rightarrow CF_2O + F$	[28,32]
14	$CF_2 + H \rightarrow CF + HF$	[27,32,33]
15	$CF_2 + O \rightarrow CFO + F$	[30]
16	$CF_2O + H \rightarrow CFO + HF$	[30,34]
17	$CF_2O + O \rightarrow CO_2 + 2F$	[30]
18	$CF + O_2 \rightarrow CFO + O$	[33,34]
19	$CF + OH \rightarrow CO + HF$	[32]
20	$CFO + CF_3 \rightarrow CF_4 + CO$	[34]
21	$CFO + H \rightarrow CO + HF$	[30,34]
22	$CFO + OH \rightarrow CO_2 + HF$	[30,34]
23	$CFO + O \rightarrow CO_2 + F$	[30,34]
24	$CO + OH \rightarrow CO_2 + H$	[32]
25	$\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2$	[30]



3. Conclusions

Thermal decomposition of BTP was investigated experimentally and theoretically in this study. Experimental results show that BTP is a relative stable extinguishing agent with a decomposition temperature around 600 °C, which were in agreement with the high apparent activation energies obtained by experimental and theoretical calculation. In a temperature range from 600 °C to 800 °C, the decomposition ratio of BTP increases with the rise in temperature, and raises noticeably by extending residence time. But, little influence was exerted by altering the initial mole fraction of BTP. The major decomposition products in a carrier gas of nitrogen were verified to be CF₃CCH and/or CF₃Br. Beyond that, we attribute its good fire extinguishing effect to Br• and CF₃• and related radicals at high temperature by removing active species from the combustion

Fig. 6. Reaction fluxes for BTP decomposition and extinguishing mechanism at high temperature.

zone catalytically. The good properties and fire extinguishing effect of BTP contribute it to be an excellent Halon replacement agent.

4. Experimental

4.1. Materials

2-Bromo-3,3,3-trifluoropropene (purity \geq 99.75% after rectification) used in this study was obtained from the reaction of CF₃CHCH₂ (g) with Br₂ (liquid) at a low temperature, followed by dehydrobromination by aqueous solution of potassium hydroxide



Fig. 7. Schematic diagram of the thermal degradation experiment system.

Table 4

GC and GC-MS operation conditions.

Parameters	GC	GC-MS
Instrument	Beifen-Ruili SP-3420A	Shimadzu GC-MS-QP2010 ultra
Column	DB-5, 30.0 m, 0.25 mm, 0.25um	Rtx-5ms, 30.0 m, 0.25 mm,0.25 μm
Carrier gas flow rate	6 mL min ⁻¹	2 mLmin ⁻¹
Column temperature	35 °C	180 °C
Injection	40 μL gas injection, split mode	40 μL gas injection, split mode
Split ratio	1:50	1:50
Injection temperature	250.00 °C	250.00 °C
Detector (FID) temperature	40 °C	
Ion source temperature		200.00 °C
Ionization method		Electron impact
Ionizing energy		70 eV
Scan range		m/z 35.0-500.00

[35,36]. Common purity nitrogen with a purity of not less than 99.5% was used as the carrier gas.

$$CF_{3}CH = CH_{2} + Br_{2} \underset{0 \pm 5 \circ C}{\overset{illumination}{\to}} CF_{3}CHBrCH_{2}Br \underset{60 \circ C}{\overset{KOH}{\to}} CF_{3}CBr = CH_{2}$$

4.2. Experimental equipments and procedures

The schematic diagram of the thermal degradation device is shown in Fig. 7. This system mainly consists of a tubular pyrolysis reactor (40.0 cm long and 1.0 cm in internal diameter) that made of nickel-copper alloy, a programmable temperature control device. and a products analysis and exhaust gas treatment system. All experiments were carried out at atmospheric pressure. The temperature of the reactor was measured and controlled by the temperature control device with three K-type sheathed thermocouples evenly distributed throughout the surface of the reactor, showing that the temperature deviation was controlled within \pm 5 °C. The temperatures used to process experiment data were provided by thermocouple d inside the reactor. During the execution of experiments, the mixture of BTP (g) and carrier gas was preheated prior to entering the tubular reactor, and the initial mole fraction of BTP and the residence time in the reactor were regulated by adjusting the flow rate of BTP and carrier gas.

Prior to the experiment, the tubular pyrolysis reactor was immersed in acetone for 2 h to get rid of impurities firstly. After drying at 110 °C in oven, the reactor was installed in the heater and was heated to 500 °C for 1 h with N₂ flow to remove contaminants. After cooling to room temperature, BTP was then injected into the reactor and the reactor was heated to 800 °C at a constant heating rate of 3 °C min⁻¹. After removal of particulates and acid gases by passing through a filter and a warm water scrubber (see Fig. 7), the gaseous degradation products were collected and then analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

4.3. Products analysis

In this study, GC and GC–MS were used to identify the decomposition products, and to quantify the decomposition ratios

of BTP. The operating conditions of GC and GC–MS are shown in Table 4. The decomposition ratios of BTP were calculated using the following formula: $\alpha = 1 - A(BTP)/A_0(BTP)$, where α (%) is the decomposition ratio of BTP, A(BTP) and $A_0(BTP)$ are the chromatographic peak areas of BTP with a constant injection sample size before and after pyrolysis severally.

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