



Degradation of brominated flame retardant in computer housing plastic by supercritical fluids

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ABSTRACT

The degradation process of brominated flame retardant (BFR) and BFR-containing waste computer housing plastic in various supercritical fluids (water, methanol, isopropanol and acetone) was investigated. The results showed that the debromination and degradation efficiencies, final products were greatly affected by the solvent type. Among the four tested solvents, isopropanol was the most suitable solvent for the recovery of oil from BFR-containing plastic for its (1) excellent debromination effectiveness (debromination efficiency 95.7%), (2) high oil production (60.0%) and (3) mild temperature and pressure requirements. However, in this case, the removed bromine mostly existed in the oil. Introduction of KOH into the sc-isopropanol could capture almost all the inorganic bromine from the oil thus bromine-free oil could be obtained. Furthermore, KOH could enhance the depolymerization of the plastic. The obtained oil mainly consisted of single- and duplicate-ringed aromatic compounds in a carbon range of C9–C17, which had alkyl substituents or aliphatic bridges, such as butylbenzene, (3-methylbutyl)-benzene, 1,1'-(1,3-propanediyl)bis benzene. Phenol, alkyl phenols and esters were the major oxygen-containing compounds in the oil. This study provides an efficient approach for debromination and simultaneous recovering valuable chemicals from BFR-containing plastic in e-waste.

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1. Introduction

The growth in electrical and electronic equipment production and consumption has been increasing drastically for the last two decades. As a result, about 20–50 million tones of electronic wastes (e-wastes) are generated worldwide every year [1]. In China, more than 2 million tons of e-wastes are generated each year, and the figure is expected to increase to approximately 5.4 million tons by 2015 [2,3]. E-wastes, thought as one of the largest sources of heavy metals and organic pollutants in municipal waste, have become a serious problem [2]. Among which, organic pollutants, mainly brominated flame retardants, have become the focus of research in recent years [4]. BFRs include tetrabromobisphenol A (TBBPA), polybrominated diphenyl ether (PBDE), hexabromocyclododecane (HBCD), etc. which are toxic to both humans and environment [5]. PBDE has been recognized as persistent organic pollutants (POPs) in 2009. Therefore, BFRs-containing plastics are thought as hazardous wastes which are problematic for treating or recycling. Currently, 96% of electrical and electronic plastics are either

dumped in landfills or incinerated without energy recovery [6]. Nevertheless, neither of the foregoing treatments are environmental benign approach since BFRs could be leached out in landfill [7] or formation of more toxic substances such as polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) during combustion [8]. Development of removal method of BFRs and recycling processes of plastic from e-wastes is urgently desired, which also meet the requirement of European Union's Directive on Waste Electrical and Electronic Equipment (WEEE) [9].

Thus far, chemical recycling was thought as an attractive recycling method of waste plastic whose products could potentially be used as fuels, raw materials or as chemical feedstock [10]. The existing method for recycling of BFRs-containing plastics is mainly pyrolysis; however, extra problems were encountered in the process which was mainly caused by BFRs. For example, high content of organo-bromine compounds existed in oil by conventional pyrolysis treatment [11]; most of the bromine and a large proportion of chlorine transferred to the oil (inorganic Br and Cl) during fast pyrolysis process [12]. The bromine in the form of organic or inorganic in oil would restrict further use of the oil. Though addition of catalyst (carbon composite of iron oxide (Fe₃O₄)) could solve these problems, it relied on large volume consumption of catalyst [13]. Additionally, catalyst poisoning may be a problem during

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scale-up of the procedure. Other disadvantages such as higher operation temperature (400–1000 °C), nonuniform heat transfer, low yields of desired products, and excessive char and gas formation also present in the pyrolysis process of plastic [14].

The other attractive method is supercritical fluid technology. Given the properties such as, low dielectric constant, low viscosities, high mass transport coefficient and high diffusivity, supercritical fluid is introduced as an environment-friendly method to chemical recycling of waste plastic recently. These unique properties confer good solvent ability for organic chemical reactions such as oxidation, gasification, liquefaction, solvolysis [15]. As a result, sc-fluids technology might overcome the disadvantages of pyrolysis mentioned above. Sub- and supercritical water has been applied to decompose BFRs-containing plastics in which an excellent debromination efficiency and bromine-free oil were obtained [16,17]. However, high critical temperature and pressure ($T_c = 374\text{ °C}$, $P_c = 22.1\text{ MPa}$) is the shortcoming of sc-water which leads to serious corrosion of reactor and higher energy consumption [18]. Organic solvents such as methanol, acetone, and ethanol are also used as supercritical fluids in chemical recycling of waste plastic. Compared with sc-water, these solvents have not only lower critical temperature and pressure (e.g., the T_c and P_c of methanol is 239.5 °C and 8.08 MPa , respectively) but also other advantages [19]. Thus far, less report is available on the treatment of BFRs-containing plastics in supercritical organic solvents. Whether the supercritical organic solvent treatment can degrade BFRs is not clear yet. In the present work, we investigated the decomposition process of waste computer housing plastic containing BFR in supercritical methanol, isopropanol, acetone and water. The objectives of the study are (1) to make clear whether sc-organic solvents can degrade BFR and BFR-containing plastic so as to obtain bromine-free oil, (2) to select appropriate solvent for the process and characterize the properties of the obtained products.

2. Experimental

2.1. Materials

Waste computer housing plastic, supplied by HuaXing Environmental Protection Company of Beijing, China, was ground to <1 mm by the combination of cutting and centrifugal mills under cooling condition by liquid nitrogen. It was identified that the plastic was made of acrylonitrile–butadiene–styrene (ABS) with TBBPA as additive flame retardant. Elemental analysis (wt%) indicated that the plastic contains: carbon 70.4%, hydrogen 6.6%, nitrogen 4.2%, bromine 7.3%, antimony 4.6% and others 6.9%. TBBPA (GR, 97%) was purchased from Acros Co., Ltd. Acetone, methanol, isopropanol and methylene dichloride (HPLC) were obtained from J.T. Baker Co., Ltd. Potassium hydroxide and other alkalis (AR) were purchased from Sinapharm Medicine Holding Co., Ltd. (Beijing, China).

2.2. Apparatus and procedure

Supercritical solvents decomposition experiments were carried out in 200 mL cylindrical autoclave made of 316L alloy in batch mode. In a typical run, 3.00 g of plastic pellets and 50 mL solvents (acetone, methanol, isopropanol, water) were charged into the reactor and sealed. Argon gas purging was adopted for ensuring an oxygen-free medium in the reactor. The reactor was heated by heating rod. It took 50–70 min to get the desired temperature where it was maintained for desired time. After the treatment, the reactor was cooled quickly by an electric fan.

Once the autoclave cooled to room temperature, the valve was opened and the gaseous phase was passed through organic solvent and then NaHCO_3 solution with the purpose of capturing

condensable organic products and inorganic bromine ion, respectively. After removing the gaseous phase, the reactor was opened. The solid and liquid mixture was removed from the autoclave and then filtrated through a pre-weighted filter paper for separation. The wall of reactor, pipes and solid on the filter paper were all extracted with solvents until all oil had been extracted. The solid and filter paper were washed by deionized water after evaporating organic reagent and then dried to a constant weight to obtain the mass of solid residue. After organic solvent in the liquid product was evaporated, 15 mL methylene dichloride and 30 mL de-ionized water were added for extracting inorganic bromine from oil using liquid–liquid extraction technique (3 times). Trace water and methylene dichloride in the oil was removed so as to obtain the mass of the oil. Usually the degradation products were composed of three phases: oil, gas and solid residue. The removed bromine content was listed as the fourth group in present research. Degradation efficiency could be calculated by the formula: Degradation efficiency (%) = $[1 - \text{mass of solid residue}/\text{mass of the feedstock}] \times 100$. Only liquid and solid phases were collected for further analysis in this study. The results are the mean value of duplicate experiments.

2.3. Analysis methods

The oil was analyzed by a gas chromatograph equipped with mass selective detector (GC/MS, Agilent 7890A/5975C, USA). HP-5 column was used. The oven program was isothermal for 2 min at 50 °C , followed by a heating rate of $5\text{ °C}/\text{min}$ to 200 °C , then a rate of $8\text{ °C}/\text{min}$ to final 280 °C and held for 2 min. The injected volume was $1\text{ }\mu\text{L}$ with split ratio of 20/1. The ion-mass spectra derived were compared to NIST spectral library and similarity indexes of >85% were used to identify the compounds.

Inorganic bromine in the gaseous phase, solid residue and oil was transferred to alkaline solution (deionized water) by absorption or extraction. The organic bromine in oil and solid residue was transferred to inorganic form using auto bomb calorimeter. The bromine content in the form of above 5 fractions was determined by potentiometric titration using silver electrode and saturated calomel electrode. Standard solution of KBr was used for calibration of the electrode response.

The morphological properties of the plastic feedstock and solid residue were examined by scanning electron microscope with energy disperse X-ray analysis (SEM-EDAX, Hitachi S-3000N, Japan).

3. Results and discussion

3.1. Degradation process of TBBPA in various sc-solvents

TBBPA was firstly subjected to sc-fluids treatment for understanding its degradation process in sc-solvents. Table 1 shows the reaction conditions and debromination efficiencies after treatment. It was found that the bromine was almost totally transferred to aqueous phase after sc-water treatment (97.6%), and it was mainly confined in the oil fraction (HBr) in methanol and isopropanol (69.2% and 63.6%, respectively) but poorly in acetone (only 46.8%). From GC/MS analysis, no TBBPA or organo-bromine compounds were found in the oil products. Phenol and 4-butyl-phenol were the major compounds in the oil derived from water treatment. However, the oils showed more complicated compositions when other three organic solvents were used. Apart from phenol and 4-(1-methylethyl)-phenol, alkyl phenols such as 2-methyl-phenol, 4-[2-(4-methoxyphenyl)propan-2-yl] phenol, 2,4-bis(1-methylethyl)-phenol and 2,4,6-tri(1-methylethyl)-phenol were presented in the oil. These

Table 1
Conditions for sc-solvents treatments of TBBPA and debromination efficiency.

Entry	Solvent type	Temperature (°C)	Time (min)	Pressure (MPa) ^a	Debromination efficiency (%)
1	Methanol	400	60	18.5	69.2
2	Isopropanol	400	60	15.8	63.6
3	Water	400	60	19.0	97.6
4	Acetone	400	60	9.4	46.8

^a Operation pressure reached at the reaction temperature in stationary state.

compounds were supposed to come from the reactions of phenol and alkyl phenols with methanol or isopropanol, indicating supercritical fluid not only supplied reaction medium for debromination but also took part in the reaction. Sc-organic solvent treatment exhibited debromination effect on TBBPA and obtained oil products without organo-bromine compounds.

3.2. Degradation of TBBPA-containing waste computer housing plastic in various sc-solvents

3.2.1. Product yields

The waste computer housing plastic containing TBBPA was treated in supercritical methanol, isopropanol, acetone and water as shown in Table 2. Solvent type greatly influenced the plastic degradation. It should be firstly pointed out that the degradation efficiency of plastic in sc-acetone treatment was significantly higher than that of other three solvents even at 300 °C. Nevertheless, the mass of liquid product was over 3.00 g as a result of difficulty in separating oil from reaction solutions which led to the data of oil and other fractions unavailable. This was potentially due to that partial volume of acetone was wrapped by molten plastic in the acetone evaporating process since ABS-Br beginning to decompose over 350 °C [11]. For each of the other three solvents, temperature was another important parameter. In general, decomposition of plastic was slow between 300 and 350 °C, and then there was a rapid decomposition stage between 350 and 400 °C. When temperature exceeded 400 °C, the degradation efficiency of the plastic tended to a slight increase or decline. Sc-water showed the highest degradation efficiency that remained the least solid residue and produced 38.0% oil and 30.9% gas at 400 °C. Sc-methanol treatment remained the most solid (33.0%) even at 420 °C and obtained 47.0% oil simultaneously. Sc-isopropanol treatment achieved the highest oil yield of 60.0% at 400 °C which was also the highest one among all experiments. As the temperature was increased to 420 °C, formation of coke resulted in a decrease in oil yield. The gas yield was low in methanol and isopropanol treatment in which around 10% and less than 5% were obtained, respectively. Bromine yields showed the effectiveness of solvents on debromination. The debromination reaction mainly took place at temperature range of 300–350 °C in sc-water treatment, but the temperature range was broader (from 300 to 400 °C) when methanol and isopropanol were used.

Piñero-Hernanz et al. [20] suggested that the degradation of polymer in supercritical solvents relied on two main steps as reaction and dissolution of polymer in the solvent, therefore the solvation capability of the solvent will be an important parameter. Polarity of the solvent was thought to be related to the solvation capability. Acetone has the highest polarity (2.85 D) among the four reagents; as a result, the highest degradation efficiency was obtained at even relative low temperature which was attributed to dissolution of polymer. For the other three reagents with similar value of dipole moment (1.70 D for methanol and isopropanol, 1.85 D for water), the sequence could be explained by the difference of dielectric constant because dielectric constant influence the solvation capability of supercritical fluid [21]. At 25 °C, the dielectric constant of isopropanol, methanol and water is 18.30, 32.61 and

80.4, respectively. They decrease to 3, 11, ~10 at 350 °C and further to 2, 9 and 1.5 when temperature was increased to 400 °C. Organics are much more soluble in solvent under supercritical region with low dielectric constant [21]; thus, the degradation efficiency performed the similar sequence as dielectric constant sequence. Additionally, the reaction in sc-water was much vigorous than that in sc-organic solvents which resulted in further decomposition of oil to gas or direct gasification of solid to gas in sc-water sharply. As a result, the most residue (37.3%), gas (31.4%) and oil (60.0%) were produced by methanol, water and isopropanol, respectively.

For the purpose of producing bromine-free oil, isopropanol was an appropriate candidate sc-solvent which got the highest oil yield (60.0%). Additionally, the pressure of sc-isopropanol is about 2 MPa less than that of methanol and water, probably as the molecule of isopropanol has 3 atoms of carbon and a higher solvation capacity to attack to the polymer more effective [20].

3.2.2. Bromine distribution

Fig. 1 shows the bromine balance of waste computer housing plastic after sc-methanol, isopropanol and water treatments. No inorganic bromine was detected in the gaseous phase in all experiments which was different from pyrolysis results that HBr mostly existed in gaseous phase [22,23]. After sc-methanol and isopropanol treatments, almost all the Br was transferred into the oils in the form of hydrogen bromide, since HBr could dissolve in alcohol and it adhered to oil when methanol and isopropanol evaporated. In the case of sc-water treatment, the dissolution of removed bromine in water resulted in the formation of hydrogen bromide.

As can be seen from Fig. 1, TBBPA had been started to decompose at 300 °C. Increasing temperature resulted in an increase of inorganic bromine in the oil (or in water) and a decrease of organic bromine in the solid residue. At 350 °C, 93.2% of Br was found in aqueous phase after sc-water treatment. For sc-isopropanol and methanol treatment, only 68.6% and 86.4% of Br was removed,

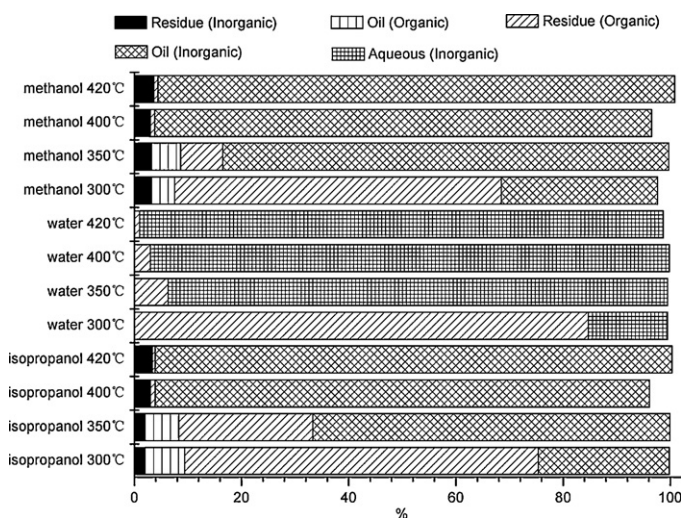


Fig. 1. Relative amount of Br in different products obtained from various sc-solvents treatment of plastic at 400 °C for 60 min.

Table 2
Yields of different fractions after sc-solvents treatment of the plastic.

Entry	Solvent type	Temperature (°C)	Pressure (MPa)	Degradation efficiency (%)	Yield (w t%) of			
					Oil	Gas ^a	Residue	Bromine
5	Methanol	300	11.0	22.0	14.0	5.6	78.0	2.4
6	Methanol	350	15.8	27.0	18.0	2.7	73.0	6.3
7	Methanol	400	20.5	62.7	40.0	15.9	37.3	7.0
8	Methanol	420	22.6	67.0	47.0	12.8	33.0	7.2
9	Isopropanol	300	6.2	12.3	8.6	1.8	87.7	1.9
10	Isopropanol	350	10.5	33.7	23.7	5.0	66.3	5.0
11	Isopropanol	400	18.0	71.3	60.0	4.3	28.7	7.0
12	Isopropanol	420	21.5	65.0	53.0	4.8	35.0	7.2
13	Water	300	4.6	7.0	3.0	2.9	93.0	1.1
14	Water	350	12.0	18.7	7.0	5.0	81.3	6.7
15	Water	400	21.0	76.0	38.0	30.9	24.0	7.1
16	Water	420	22.5	79.3	40.7	31.4	20.7	7.2
17	Acetone	300	6.0	64.3	– ^b	–	35.7	–
18	Acetone	350	8.2	80.3	–	–	19.7	–
19	Acetone	400	11.6	81.7	–	–	18.3	–
20	Acetone	420	12.5	72.3	–	–	27.7	–

^a Gas = 100 – (oil + residue + bromine).

^b Unavailable.

respectively. Additionally, it was worth noting that 5.4% and 6.3% of Br in the form of organo-bromine compounds in oil was detected at this temperature. When temperature increased to 400 °C or higher, over 95.2% of bromine was removed by sc-methanol and isopropanol treatment and no organic bromine was found in the oil.

It can be inferred that flame retardant was primarily extracted by supercritical fluids, and then it decomposed in the medium. For example, in the case of sc-water treatment at 350 °C, 93.2% of bromine was found in aqueous phase but 81.3% of plastic remained. This was in agreement with Md. Azhar Uddin's results that debromination had almost finished before degradation of HIPS in subcritical water below 280 °C [24]. When temperature increased to ≥ 400 °C, the extraction and decomposition of BFR overlapped with depolymerization of plastic because plastic also decomposed to a large extent at this temperature.

Different from TBBPA degradation results that only 69.2% and 63.6% of inorganic bromine was released, over 95.2% of inorganic bromine was detected when waste computer housing plastic was decomposed in sc-methanol and isopropanol under the same condition. Polymer, for example, polypropylene (PP) was used as reductive agent for debromination of TBBPA or brominated plastic [24,25]. In the process of debromination, plenty of hydrogen produced by scission of PP reacted with bromine radicals, which promoted the debromination reaction by formation of HBr. In the present study, the plastic acted as a reductive agent for supplying hydrogen which resulted in the formation of more HBr than other compounds compared with pure TBBPA degradation. As a result, more inorganic bromine was detected in plastic degradation experiments.

3.2.3. Analysis of the oil

The oils were yellow in colour and were very viscous at 300 and 350 °C. It turned dark brown with a strong aromatic odour and the viscosity reduced a lot at 400 and 420 °C. The oils were further analyzed by GC/MS so as to understand their organic compositions.

According to bromine balance analysis, flame retardant degraded prior to the decomposition of plastic at temperature below 350 °C. This was also confirmed by GC/MS results of the oil. The oil derived from sc-water, methanol and isopropanol treatment at 350 °C mainly comprised of phenol, alkyl phenols, bisphenol A, as well as brominated phenols. These compounds came from the degradation of TBBPA. Especially for water treatment, phenol and alkyl phenol accounted for 78.3% of the product. TBBPA was

detected in the oil derived by sc-acetone treatment at 350 °C, indicating debromination of TBBPA in sc-acetone was not effective as others.

Fig. 2 illustrates the GC/MS chromatograms of the oils obtained at 400 °C and Table 3 presents the list of the possible compounds. The chromatograms showed the product categories and abundance were greatly affected by the solvent type. The oil obtained by sc-acetone treatment was totally different from those obtained by other three solvents treatment. In the oil, 1,3,5-trimethyl-benzene was the major compound and followed by 2,4,6-trimethyl-pyridine; however, it is really a difficult task to propose a possible mechanism for the formation of the two compounds. For other three solvents treatment, the major compounds in oils could be divided into three groups namely: the early eluting mono-benzene ring range (5.00–25.00 min), the middle clusters with diphenyl-skeletons or mono-benzene ring with long branches (25.00–32.00 min), and the late eluting complicated compounds (32.00–44.00 min). The oil obtained by sc-isopropanol treatment mainly comprised of compounds with mono-benzene ring such as, butyl-benzene, 1-methylbutyl-benzene, 1,1'-(1,3-propanediyl)bis benzene was the single largest

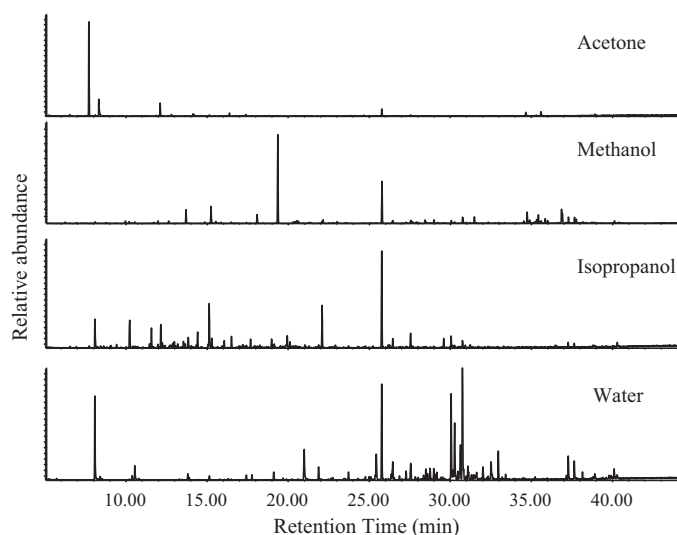


Fig. 2. Typical GC/MS chromatogram of oils obtained from various sc-solvents treatment of plastic at 400 °C for 60 min.

Table 3
Main components of the oil identified by GC/MS (% area).

R.T. (min)	Compound name	Solvent			
		Acetone	Methanol	Isopropanol	Water
7.72	Benzene, 1,3,5-trimethyl-	53.31	– ^a	0.57	–
8.10	Phenol	0.87	0.54	5.49	8.20
8.32	Pyridine, 2,4,6-trimethyl-	13.21	–	–	0.52
10.20	Phenol, 2-methyl-	–	0.51	–	–
10.23	Benzene, butyl-	–	–	6.14	–
11.57	Benzene, (1-methylbutyl)-	–	–	3.38	–
11.98	Benzene, 1-methyl-2-(2-propenyl)-	–	2.47	–	–
12.11	2-Cyclohexen-1-one, 3,5,5-trimethyl 1-	9.26	–	–	–
12.15	Benzene, (3-methylbutyl)-	–	–	3.13	–
13.54	Benzene, (1-methyl-1-butenyl)-	–	–	1.03	–
13.70	3-Phenyl-1-propanol, acetate	–	3.80	–	–
13.84	Benzene, 1-methyl-2-(1-methyl-2-propenyl)-	–	–	1.82	–
14.15	Benzene, 1,4-dimethyl-2-(2-methylpropyl)-	1.55	–	–	–
15.15	Phenol, 4-(1-methylethyl)-	0.76	–	9.65	0.52
15.24	Benzenepropanol	–	5.16	–	–
15.29	Benzene, (1,3-dimethyl-2-butenyl)-	–	–	1.60	–
16.06	Benzene, (1-propylbutyl)-	–	–	1.25	–
16.38	Benzene, 1,3,5-trimethyl-2-(1-methylethenyl)-	1.87	–	–	–
16.51	Benzene, 1-methoxy-4-pentyl-	–	–	2.05	–
18.08	Benzenebutanenitrile	–	2.76	–	–
19.36	Benzenebutanoic acid, methyl ester	–	26.01	–	–
19.94	Phenol, 2,5-bis(1-methylethyl)-	–	–	2.71	–
22.09	Benzenebutanoic acid	–	1.05	7.38	–
25.43	5-Methyl-3-phenylcyclopent-2-en-1-one	–	–	–	3.04
25.78	Benzene, 1,1'-(1,3-propanediyl)bis	4.87	12.42	18.30	9.99
26.45	Benzene, 1,1'-(1-methyl-1,3-propanediyl)bis-	–	–	–	2.45
27.55	Bicyclo[4.2.1]nona-2,4,7-triene, 7-phenyl-	–	–	2.75	–
27.56	1,2-Diphenylcyclopropane	–	1.03	–	2.12
28.49	Benzene, 1,1'-(2-methyl-2-propenylidene)bis-	–	–	–	1.06
28.75	Benzene, 1-methyl-2-phenoxy-	–	–	–	1.30
28.98	Benzene, 1,1'-(1-butenylidene)bis-	–	–	–	1.06
28.99	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	–	1.08	–	–
30.05	Benzene, 1-methoxy-4-(phenylmethyl)-	–	–	2.06	–
30.10	Benzene, 1,1'-oxybis[3-methyl-	–	–	–	8.72
30.27	Naphthalene, 1,2,3,4-tetrahydro-1-methyl-	–	–	–	6.59
30.63	Benzene, (1-methyldecyl)-	–	–	–	4.68
30.75	1,5-Diphenylhex-3-ene	–	–	–	14.45
31.49	Hexadecanoic acid, methyl ester	–	2.01	–	–

^a Not detected.

compound and followed by phenol and 4-(1-methylethyl)-phenol. The oil derived by sc-water treatment was mainly composed of the middle clusters such as, 1,1'-(1,3-propanediyl)bis benzene, 1,5-diphenylhex-3-ene. In the case of sc-methanol treatment, apart from 1,1'-(1,3-propanediyl)bis benzene and benzenebutanoic acid, methyl ester as the major compounds, there was also a cluster of late eluting complicated compounds with 3 benzene rings such as m-terphenyl.

The compounds were further analyzed by category in each of the oils as shown in Table 4. The compounds with peak area >0.5% and the structure was identified made up 64–68.7% of the oils. Aromatics accounted for 26% of the total products in methanol derived oil which were mainly distributed in >C13. There was around 42% aromatics in the oil attained by water treatment and they were the compounds with carbon number >13 (42%). Aromatics also accounted for 42% of the oil obtained by isopropanol treatment but it was worth noting that 19% of the aromatics were distributed in C5–C13. Apart from aromatics, plenty of oxygen-containing compounds were found in the oils. 40% of the products were such kind of compounds in methanol derived oil and about 22% were presented in oils obtained by sc-isopropanol and water treatment. Nitrogen-containing compound such as benzenebutanenitrile was found in some derived oils. It presented in methanol derived oils with concentration of around 3.0% at all temperatures. No nitrogen-containing compound was found in oils obtained by sc-isopropanol and water treatment at 400 °C.

It was suggested that free radicals reaction was the polymer decomposition mechanism in sc-fluids [26]. When the energy provided by the reaction system is greater than the bond energy of the polymer, the free radicals are produced through bond broken. Free radical reaction leads to the decomposition of polymer by the chain initiation, growth and termination. Consequently, low-molecular fragments from random scission of polymer are produced, and then they are continuously depolymerized to smaller molecules. The termination reaction of chain can be either between small-molecular radicals with hydrogen radical or between small-molecular radicals. Toluene, ethyl benzene and styrene (C6–C9) took up a large proportion in the oil by pyrolysis or hydrolysis of ABS-Br [11,17]. In the present study, the content of such compounds were low but the concentration of 1,1'-(1,3-propanediyl)bis benzene was relatively high. We proposed that combination of toluene radical and ethyl benzene or styrene radical would yield 1,1'-(1,3-propanediyl)bis benzene, therefore toluene, ethyl benzene and styrene were consumed. Oxygen-containing compounds in methanol derived oil such as benzenepropanol could be formed from reaction of methanol with styrene [27]. Benzene-propanol again reacted with methanol to form benzenebutanoic acid, methyl ester. Such serious methylation reaction resulted in the formation of more oxygen-containing compounds in sc-methanol (40%). Though the reaction of isopropanol with the degradation products also took place, it was not as serious as methanol potentially because of steric effect of isopropanol with 3 carbon atoms.

Table 4

Compounds found in the oil obtained at 400 °C (% area).

		Acetone	Methanol	Isopropanol	Water
Aromatics	C6–C9	53.31	– ^a	0.57	–
	C10–C13	13.31	2.47	19.15	<1
	>C13	4.87	23.73	22.30	42.40
	Total	71.49	26.20	42.02	43.40
Oxygen-containing compounds		10.89	39.71	21.96	21.78
Nitrogen-containing compounds		13.21	2.76	–	–
Others ^b		5.41	31.33	36.02	34.32

^a Not detected.^b Peak area <0.5% or unidentified.

3.2.4. Characterization of the solid residue by SEM and EDAX

The SEM micrographs of feedstock and the solid residue obtained at 400 °C for 60 min treatment and EDAX spectra of solid residue obtained by sc-isopropanol treatment are shown in Fig. 3. The surface of the plastic feedstock was compact and smooth. After sc-water treatment, the surface became rough that huge amounts of nearly spherical particles and small gaps could be seen, which was similar to a network with “coral type” structure. The “coral type” structure was also presented in the solid residue after sc-methanol and isopropanol treatment, but plenty of macro pores appeared inside the solid residue. The enhancement of plastic decomposition by sc-fluids was believed to be due to dissolution of high molecular weight hydrocarbons into sc-fluid and diffusion of fluid into the molten plastic phase. Thus, the “coral type” structure was formed by the reaction of fluids with plastic and macropores were caused by swelling of organic solvents. These effects accelerated the extraction of BFR and depolymerization. Nevertheless, in the case of sc-acetone treatment, macro pores existed but the surface was smooth and “coral type” structure was not as obvious as others. This meant that degradation reaction was not as vigorous as that in other three solvents and the dissolution of plastic into acetone played the lead role in degradation of plastic. EDAX spectra of solid obtained by isopropanol treatment shows that the typical bromine peak almost disappeared, indicating that the extraction of BFRs from plastic was completely.

3.3. Effect of catalyst addition on plastic degradation in sc-isopropanol

Isopropanol was an ideal solvent for producing oil from BFR-containing plastic; however, the removed bromine almost totally existed in the oil after evaporating isopropanol. In this section, 3 kinds of alkalis (Ca(OH)₂, NaOH and KOH) and 2 kinds of alkaline salts (NaHCO₃ and Na₂CO₃) were added to sc-isopropanol because of the following reasons. First of all, salt such as NaCl can dissolve in supercritical alcohol and it precipitates once supercritical condition return to ambient condition, thus we presumed that the inorganic bromine would be removed from isopropanol solution using the unique property of supercritical isopropanol through adding alkali or alkaline salt. The second, alkali or alkaline salt can promote debromination reaction [16,17]. The third, alkali catalyst can directly increase the depolymerization rate of plastic in sc-alcohol [20].

3.3.1. Effect of additives on product yields

The product yields after adding alkalis and alkaline salts are shown in part of Table 5 (Entries #22–26). It was found that KOH exhibited eminent performance for decomposition of the plastic and followed by NaOH. Nevertheless, addition of Ca(OH)₂, NaHCO₃ and Na₂CO₃ exhibited negative effects on oil recycling as only around 20% oil were obtained. In the case of Ca(OH)₂, up to 69.7% of

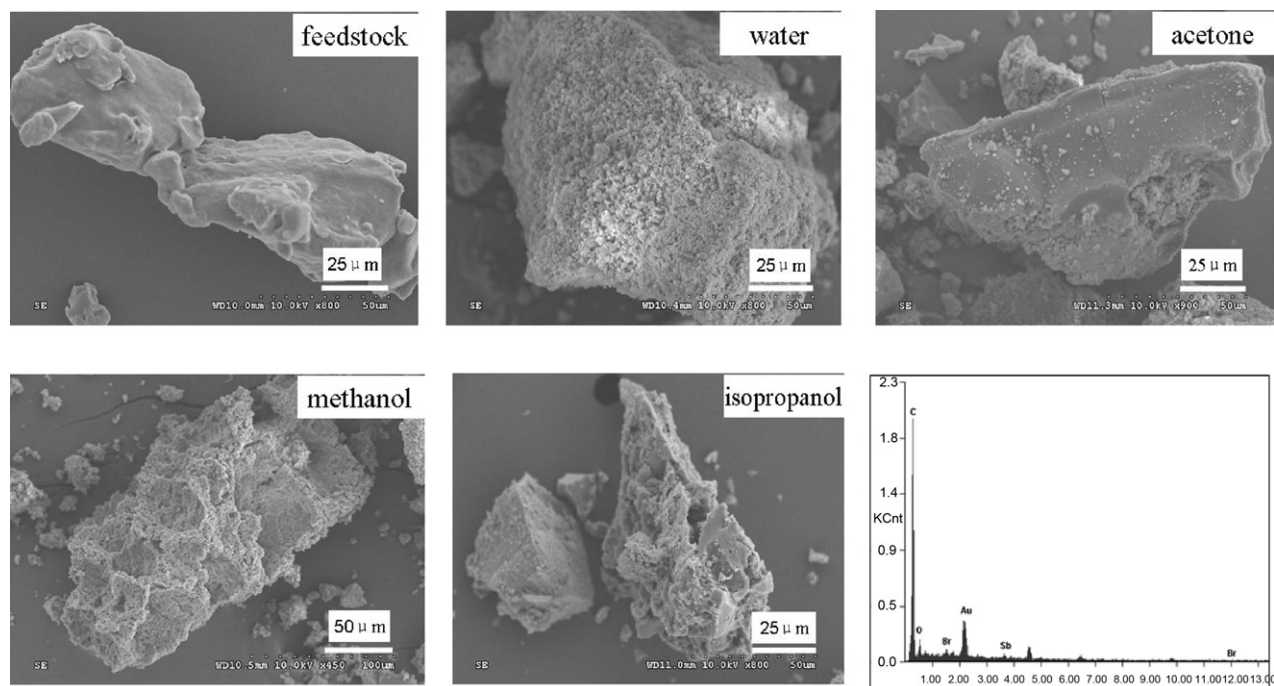


Fig. 3. SEM micrographs of feedstock and the solid residue obtained at 400 °C for 60 min treatment and EDAX spectra of solid residue obtained by sc-isopropanol treatment.

Table 5
Yields of different fractions after sc-isopropanol treatment of the plastic in the presence or absence of additives.

Entry	Additive	Mass (g)	Temperature (°C)	Time (min)	Pressure (MPa)	Degradation efficiency (%)	Yield (wt%) of			
							Oil	Gas	Residue	Bromine
21		0	375	60	14.5	54.5	40.7	7.5	45.5	6.2
22	NaOH	0.18	375	60	11.6	57.0	42.7	8.7	43.0	5.7
23	KOH	0.18	375	60	12.2	66.0	51.0	9.1	34.0	5.9
24	Ca(OH) ₂	0.18	375	60	12.5	30.3	21.7	4.7	69.7	4.0
25	Na ₂ CO ₃	0.18	375	60	13.2	46.3	26.3	16.3	53.7	3.7
26	NaHCO ₃	0.18	375	60	13.6	48.3	22.7	21.0	51.7	4.6
27	KOH	0.09	350	60	8.1	35.0	21.0	8.9	65.0	5.1
28	KOH	0.18	375	120	12.4	73.0	54.0	12.6	27.0	6.4
29	KOH	0.30	375	60	12.2	68.7	53.2	8.9	31.3	6.6
30	KOH	0.18	400	30	13.2	74.0	57.9	10.0	26.0	6.1
31	KOH	0.18	400	60	13.6	76.0	64.0	5.2	24.0	6.8
32	KOH	0.30	400	60	13.4	74.7	62.1	5.5	25.3	7.1

plastic remained after treatment. NaHCO₃ and Na₂CO₃ performed similar effect on degradation potentially because they have similar properties. Since KOH and NaOH can dissolve in sc-isopropanol and other 3 additives are not soluble, it could be considered that homogenous catalytic system was important. Bromine yield also confirmed this point. KOH and NaOH performed higher bromine yield (5.7% and 5.9%, respectively) than the other 3 additives (3.7–4.6%). Accordingly, KOH was chosen as the catalyst. Additionally, the pressure decreased by 2.1–4.8 MPa after addition of KOH.

Degradation of the plastic was affected by the dosage of KOH and reaction time as shown in part of Table 5 (Entries #27–32). Low dosage of KOH (0.09 g) to isopropanol had negligible influence on polymer degradation at 350 °C. As the temperature was increased to 375 °C and the dosage of KOH increased to 0.18 g, 51.0% oil was obtained; comparatively, only 40.7% oil was attained in the absence of KOH. Nevertheless, longer reaction time to 120 min or larger dosage of KOH to 0.30 g did not produce more oil at this temperature. At 400 °C, 57.9% oil generated after 30 min treatment, and additional 6% was attained when 60 min was employed. Given the parameters of temperature, time and catalyst, it was considered that 64% was the maximum oil yield in sc-isopropanol treatment of this plastic (obtained at 400 °C for 60 min in the presence of 0.18 g KOH).

3.3.2. Effect of KOH on bromine distribution

The marked influence of KOH addition was that it changed the bromine distribution as shown in Fig. 4. Inorganic bromine in oil transformed to solid residue. It was realized through the neutralization reaction of HBr with KOH forming KBr, because the salt

would precipitate from isopropanol once the supercritical condition returned to ambient condition. The content of bromine fixed on solid residue depended on the dosage of KOH which accorded with stoichiometric ratio of the reaction. The dosage of 0.30 g was enough for capturing all bromine. Consequently, 84.5% and 94.0% of bromine was fixed at 375 °C and 400 °C, respectively, and only 2.3% of Br remained in oil at 400 °C. Thus the bromine could be removed easily by water extraction of the solid residue. Nevertheless, addition of KOH had limited effect on promoting debromination reaction. This could be explained as following: KBr can dissolve in supercritical isopropanol, thus the equilibrium of the neutralization reaction was not altered. As a result, the debromination efficiency had no increase in the presence of KOH. This was different from that using supercritical water in which reducing of resultant (caused by salt deposition from sc-water) promoted the debromination reaction [16,17].

3.3.3. Effect of KOH on oil composition

Addition of KOH had minor influence on oil composition compared with the oil obtained in the absence of KOH according to GC/MS results. After adding KOH, the kinds of compounds reduced. In addition, benzenebutanoic acid and 1,1'-(1,3-propanediyl) bis-benzene were the major products. The two compounds accounted for 22.8% and 20.7% of the oil, respectively, which were higher than that in the oil obtained in absence of KOH.

4. Conclusions

The results of this study showed that supercritical fluid process was an efficient approach for debromination and simultaneous decomposition of BFR-containing plastic for recycling bromine-free oil. The debromination efficiencies of the four types of tested fluids followed the sequence of water > methanol > isopropanol > acetone. Over 90% of bromine was removed in subcritical water at 350 °C, but the temperature should be increased to 400 °C for sc-methanol and sc-isopropanol to achieve similar debromination efficiency. For oil recovery, the temperature should be ≥400 °C, and the oil yields were in the sequence of isopropanol > methanol > water > acetone. Among the four solvents, sc-isopropanol treatment obtained the highest oil product (60%), and furthermore, this solvent exhibited excellent effect on the degradation of brominated flame retardant. Addition of KOH into sc-isopropanol did not enhance bromine removing, but captured almost all the bromine from the oil and thus bromine-free oil was obtained. The oil was identified as a mixture of aromatics (42%) and oxygen-containing compounds (21%) such as benzene derivatives and phenols, which could be separated for recovery of phenols and other chemicals or used as fuel.

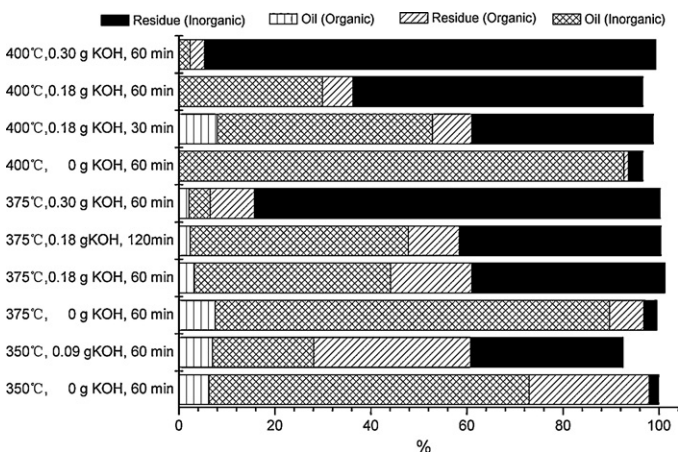


Fig. 4. Relative amount of Br in different products obtained from sc-isopropanol treatment of plastic in the presence or absence of KOH.

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