

Study on the degradation of brominated flame retardants in waste circuit boards using a supercritical fluid method: methodology, influencing factors, and optimal fluid type

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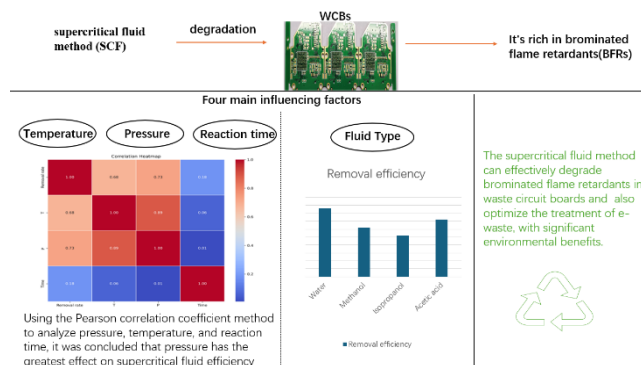
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Graphical abstract



Abstract

The supercritical fluid (SCF) method is recognized as an environmentally friendly and efficient technology for the degradation of brominated flame retardants (BFRs) in waste circuit boards (WCBs). This study provides a detailed exploration of the SCF definition, the principles of debromination, and the key factors influencing the degradation process. Additionally, the selection process for the optimal supercritical fluid is thoroughly discussed. Comprehensive analysis reveals that temperature, pressure, reaction time, and the choice of fluid significantly impact the degradation efficiency. The study identifies the optimal supercritical fluid and highlights the most critical influencing factors, offering technical support and theoretical guidance for the effective treatment of BFRs in WCBs.

Keywords: Supercritical fluid method, brominated flame retardants, waste circuit boards, debromination factors

1. Introduction

As living standards have improved, electronic products have become essential in daily life. However, this increased dependence has resulted in a significant rise in e-waste due to more frequent replacements. In 2021

alone, 208 million units of televisions, washing machines, refrigerators, and computers were discarded. By 2030, global e-waste is projected to reach approximately 74 million tons (Forti, V., *et al.* 2020).

Circuit boards, which serve as the backbone for electronic components and connections, are primarily composed of various metals. Key metals in circuit boards include copper, iron, aluminum, lead, tin, titanium, antimony, zinc, manganese, gold, silver, and cadmium. Additionally, circuit boards contain brominated flame retardants (BFRs), a group of brominated organic compounds essential for fire resistance (Ge, X., *et al.* 2023). Common BFRs in electronic products include tetrabromobisphenol A, bromophenols, polybrominated diphenyl ethers (PBDEs), and various aliphatic and brominated oligomers and polymers (Luo, K., *et al.* 2023).

BFRs are known for their excellent flame-retardant properties (Wu, H., *et al.* 2023) and are widely used in plastics and textiles (Dong, Y., *et al.* 2023). However, at high temperatures, BFRs can decompose, producing hazardous by-products such as dioxins, benzofurans, and corrosive gases like hydrogen bromide and hydrogen chloride (Van Yken, J., *et al.* 2021). Once released into the environment, BFRs undergo various processes, including adsorption, desorption, photodegradation, and microbial degradation, leading to the formation of lower-brominated, hydroxylated, and methoxylated congeners. These derivatives have higher mobility and increased toxicity, posing serious risks to animal and plant growth, human reproductive health, and neurological and endocrine systems (Yu, F., *et al.* 2021). Furthermore, improper disposal or incineration of BFR-containing materials can significantly degrade air quality and cause extensive pollution to land and ecosystems. As a result, pentabromodiphenyl and octabromodiphenyl ether were added to the global list of controlled substances under the Stockholm Convention in 2009, with decabromodiphenyl ether added in the 2017 amendment (Abbasi, G., & Li, L.,

2019). This highlights the growing necessity to transition toward halogen-free and environmentally friendly alternatives to BFRs.

In recent years, SCF technology has emerged as a promising and environmentally sustainable method for degrading BFRs. SCF technology offers distinct advantages, including a low dielectric constant, high mass transfer coefficient, and high diffusion rate, making it

Table 1. Composition of WCBs %

	Formation	Concentration	Non-metallic	Refractory	Composition	Concentration
Metal	Cu	20	50~72(Faraji, F., <i>et al.</i> 2022)	Oxide	Si	15
	Zn	1			Al ₂ O ₃	6
	Al	2			Alkaline earth metal oxide	6
	Pb	2			Others	3
	Ni	2			Total oxides	30
	Fe	8			Nitrogenous polymers	30
	Sn	4			C-H-Opolymers	25
	Other metals	1			Halogenated polymers	4
	Total metals	28~40			Total plastics	30
						Plastics

particularly effective (Peyrin, E., & Lipka, E. 2024). Moreover, SCF has shown potential as an efficient, cost-effective, and controllable solution for treating Waste Electrical and Electronic Equipment (WEEE), outperforming traditional methods (Gripon, L., *et al.* 2021a).

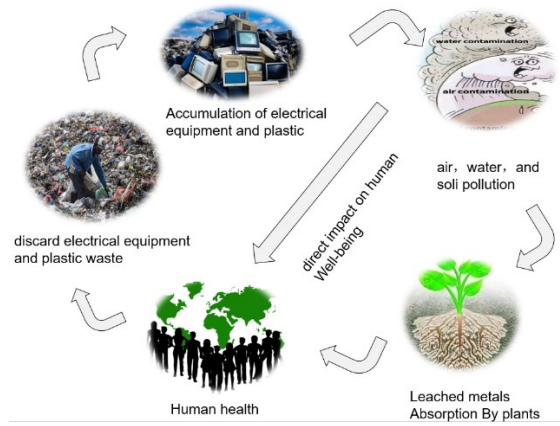


Figure 1. Hazards to human health and the environment caused by improper disposal of WCBs

This paper addresses the following key aspects: The first section defines and explains the principles of SCF technology, providing an in-depth overview of typical SCF methods with a focus on their application to debromination. The subsequent section delves into the underlying mechanisms of these methods and examines the influence of critical factors. Finally, the paper compares the effectiveness of four commonly used debromination fluids, evaluating the advantages of the most efficient one.

In summary, this study investigates the application of debromination techniques for BFRs, analyzing the impact of various factors and fluid types on debromination efficiency. The findings identify pressure as the most critical factor and highlight water as the most effective fluid for achieving optimal debromination. By establishing a scientific basis for evaluating beneficial debromination factors, this research supports further exploration of different fluids and offers strategies for environmentally sustainable BFR treatment.

2. Research methodology and data sources

This study analyzed 108 datasets derived from articles published between 2003 and 2023. Key parameters were

selected as independent variables and analyzed using Pearson's correlation coefficient. To ensure uniformity and enhance the accuracy of the correlations, data normalization was applied. The normalization formula used is as follows:

$$\text{normalization} = \frac{X_i - X_{\min}}{X_{\max} - X_{\min}}$$

X_i : original data

X_{\min} : the minimum value

X_{\max} : the maximum value

In Pearson correlation analysis, for two variables (x) and (y) , a set of data can be obtained through experimentation, denoted as (X_i, Y_i) ($i = 1, 2, \dots, n$). The Pearson's correlation coefficient (r) is calculated using the following expression:

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}}$$

\bar{X}, \bar{Y} : the means of the n test values, respectively

X_i : The data point in the dataset X

Y_i : The data point in the dataset Y

\bar{x} : Verage of X

\bar{y} : Verage of Y

The value of (r) ranges from -1 to +1. A positive (r) indicates a positive correlation between the variables, while a negative (r) indicates a negative correlation. The closer the absolute value of (r) is to 1, the stronger the correlation. An (r) value of 0 indicates no linear correlation between the variables. Generally, a correlation coefficient between 0 and 0.2 suggests no or very weak correlation; 0.2 to 0.4 indicates weak correlation; 0.4 to 0.6 indicates moderate correlation; 0.6 to 0.8 indicates strong correlation; and 0.8 to 1 indicates very strong correlation.

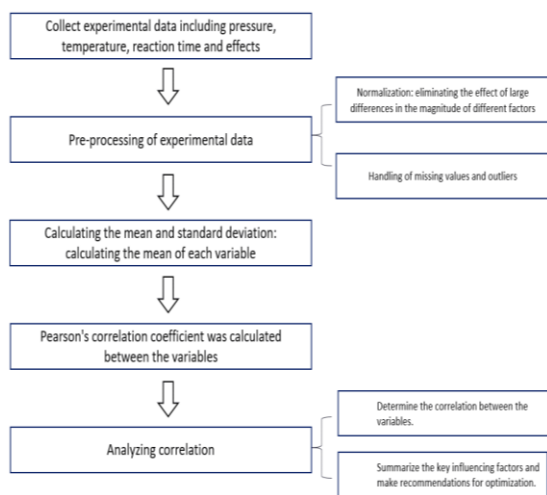


Figure 2. The process of the research

The literature for this review was sourced from the Elsevier and Web of Science databases. As of April 2024, searching the keyword "BFRs" yielded 11,942 documents on Elsevier and 5,971 on Web of Science. Including

Table 2. Physical properties of SCF

physical property	Data range	note
densities	0.2-0.5 g/ml (Savage, P. E., et al. 1995)	It depends on the substance, as well as the experimental temperature and pressure.
stickiness	0.01-0.03 Pa·S	It close to that of an ordinary gas and depends mainly on temperature and pressure.
diffusion coefficient	0.2×10^3 - 0.7×10^3 (Li, K., & Xu, Z. 2019a)	It reflects its mass transfer performance and significantly larger than that of ordinary liquids (Brunner, G. 2005)

Table 3 Physical properties of SCFs, gases and liquids (Li, K., & Xu, Z. 2019b)

Physical property	Gas	SCF	SCF	Fluids
	Normal temperature, normal pressure	TcPc	Tc4Pc	Normal temperature, normal pressure
Density g/ml	$0.6 \sim 2 \times 10^{-3}$	0.2~0.5	0.4~0.9	0.6~1.6
stickiness /cms	$1 \sim 3 \times 10^{-4}$	$1 \sim 3 \times 10^{-4}$	$3 \sim 9 \times 10^{-4}$	$(0.2 \sim 3) \times 10^{-2}$
diffusion coefficient cm ² /s	0.1~0.4	0.7×10^{-3}	0.2×10^{-3}	$0.2 \sim 3 \times 10^{-5}$

3.2. Principles of SCF technology, typical methods, and debromination principles

3.2.1. Principle of SCF technology

SCF technology utilizes fluids under supercritical conditions to extract, separate, or react with various substances. This method benefits from rapid kinetics and high reaction rates, making it a prominent area of

"WPCB" reduced these to 240 on Elsevier and 13 on Web of Science. Further refinement with the keyword "debromination" narrowed the search to 73 documents on Elsevier and 10 on Web of Science. Finally, a search for "SCF technology" yielded 25 documents on Elsevier, with 63 documents selected for inclusion in this paper.

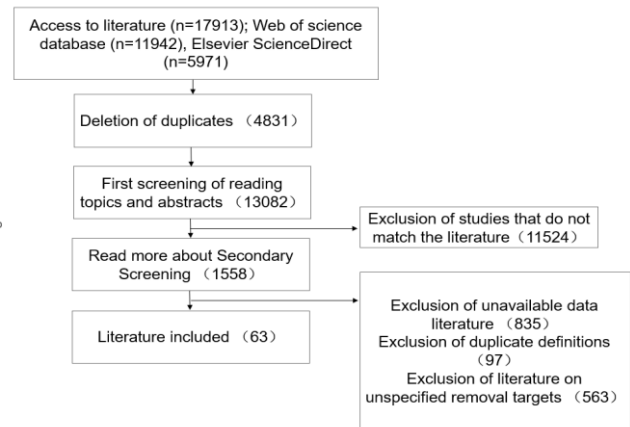


Figure 3. Criteria for literature selection and exclusion

3. Supercritical fluid method

3.1. Definition of supercritical fluids

When both temperature and pressure exceed their critical points, a substance enters a supercritical state, which exhibits distinct properties from both the gas and liquid phases (Rojas, A., et al. 2024). In this state, the substance does not adhere strictly to the characteristics of either phase but instead displays unique properties that blend aspects of both.

research and application. Typically, raw materials, such as electronic or plastic waste, are introduced into a reactor. Under controlled supercritical conditions, the desired product is separated from the solid residue, potentially yielding gaseous or liquid fuels (Preetam, A., et al. 2023). The principle of SCF technology relies on the following four key aspects:

Firstly, Supercritical State Characteristics: In the supercritical state, the fluid exhibits properties that bridge those of both liquids and gases. This state is characterized by enhanced density and solubility, high diffusivity, and low surface tension. Common SCF fluids include water, carbon dioxide, ethane, acetic acid, and ethanol (Li, K., & Xu, Z. 2019c).

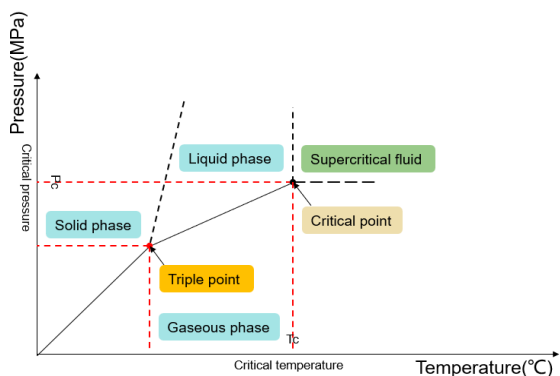


Figure 4. Schematic phase diagram of the substance

Secondly, Versatility in Solubility: SCFs can dissolve a wide range of compounds, both polar and non-polar, making them highly effective for extraction processes.

Thirdly, Adjustability: The density, solubility, and chemical properties of SCFs can be adjusted by varying temperature and pressure, allowing for selective extraction and precise control over the reaction process and resulting products.

Fourthly, Reduction of Toxic Substances: SCFs typically avoid the use of organic solvents and operate under mild conditions, reducing the production of toxic substances.

Given these principles, SCFs have been extensively used in drug extraction and material synthesis, with promising applications in the chemical industry, environmental protection, and other fields.

3.2.2. Typical methods for SCFs

SCF methods are primarily categorized into oxidation and extraction technologies.

Oxidation Process: This process involves four main steps: heating and pressurization, oxidation reaction, separation of metallic elements and inorganic salts, and decompression with heat recovery (Sun, J., *et al.* 2011). It offers advantages such as simplicity, speed, and the elimination of mass transfer limitations. Under optimal temperature and pressure conditions, organic matter can be fully removed, making it suitable for oxidizable compounds. Additionally, the process minimizes environmental impact by avoiding harmful substances like nitrogen oxides, sulfides, and dioxins (Kritzer, P., & Dinjus, E. 2001).

Extraction Process: The extraction process consists of heating and pressurization, extraction, and decompression and separation. Two common methods are employed:

Firstly, Complexing Agent Method: A complexing agent is introduced into the fluid to continuously extract target ions from the sample. After decompression, the complexing agent is separated from the fluid.

Secondly, Mixed Agent Method: Ions are mixed with an excess of the agent, followed by continuous extraction of the complex. The first method is more effective but operationally challenging. Compared to traditional extraction techniques like distillation and liquid-liquid extraction, this approach offers higher separation efficiency and reduced energy consumption due to the absence of phase transitions.

3.2.3. Principles of debromination using SCFs

The mechanism of bromine removal through SCF technology can be summarized as follows (Li, K., & Xu, Z. 2019d)

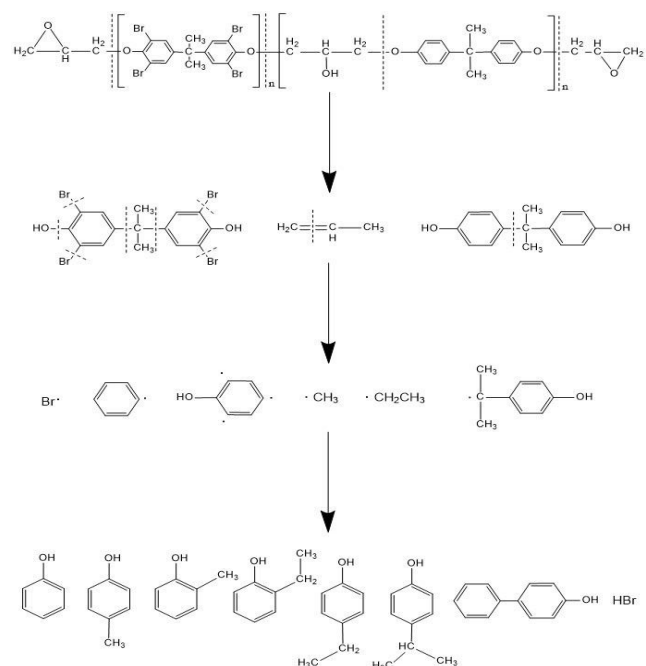


Figure 5. The mechanisms of bromine removal by SCF technology

SCF extraction for debromination involves adjusting the pressure or temperature of SCFs to alter their density and solubility. Bromine is separated based on factors such as polarity, boiling point, and molecular mass (Rao, A., *et al.* 2014). During the dissolution of BFRs, SCF oxidation debromination occurs, allowing close molecular contact within a homogeneous phase and overcoming interfacial transport limitations. This process converts the bond between alpha and beta carbons into a double bond, forming hydrocarbons and effectively removing oxidizable substances, leading to successful bromine separation (Ploeger, J. M., *et al.* 2006).

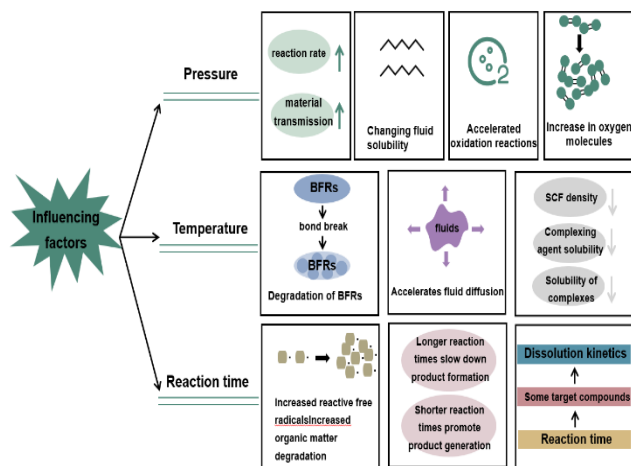


Figure 6. The mechanisms for influencing factors in SCF technology

4. Analysis of factors affecting debromination by SCF

When the condition reaches the critical point, the change of external conditions will affect the effect. The research shows that the main factors are pressure, temperature and reaction time (Li, Y., *et al.* 2024a). We will summarize and analyze the influence mechanisms of the three factors separately.

4.1. Pressure

Pressure influences bromine removal in two primary ways:

Firstly, Enhanced Extraction: High pressure improves contact between the fluid and solid sample, increasing the mass transfer rate and enhancing extraction efficiency.

Secondly, Modified Polarity and Solubility: Pressure adjustments alter the polarity and solubility of the fluid, improving selectivity and purity by more effectively distinguishing between target and non-target components (Fujii, T., *et al.* 2014).

Pressure also affects oxidation, as higher pressures can increase the concentration of oxygen molecules and the frequency of collisions, thereby speeding up the reaction (Figueroa, A., *et al.* 2022). For instance, Layla *et al.* observed a 23.3% increase in debromination efficiency of TBBPA with supercritical CO₂ when pressure was raised from 50 MPa to 70 MPa, maintaining a reaction time of 360 minutes and a temperature of 40°C (Gripon, L., *et al.* 2021b).

4.2. Temperature

Temperature affects bromine removal in three main ways:

Firstly, Bond Breaking: Higher temperatures provide sufficient energy to break bonds in BFRs, resulting in significant degradation.

Secondly, Enhanced Diffusion: Increasing temperature enhances the diffusion of fluid molecules (Chang, S., & Liu, Y. 2007).

Thirdly, Decreased Fluid Density and Solubility: Higher temperatures reduce the density of the fluid and the solubility of complexing agents and metal complexes,

increasing uncertainties with rising temperatures (Dong, X., *et al.* 2015a).

Soler (Soler, A., *et al.* 2017) investigated the effect of temperature on BFR decomposition and found that debromination efficiency increased from 18.5% to 63.6% as the reaction temperature rose from 225°C to 275°C with a reaction time of 180 minutes and pressure of 30 MPa.

4.3. Reaction time

Reaction time influences bromine removal in three main ways:

Firstly, Radical Formation: Longer reaction times generate more active radicals, enhancing the degradation efficiency of organic matter (Li, Y., & Duan, Y., 2024b).

Secondly, Reaction Equilibrium: Extended reaction times may lead to equilibrium, slowing product formation. Shorter reaction times may drive the reaction more towards product formation.

Thirdly, Dissolution Kinetics: Longer reaction times allow for more extensive dissolution, especially for compounds not readily soluble in shorter timeframes (Vogel, F., *et al.* 2005).

However, extending reaction time beyond a certain point may not improve removal rates due to decreased reactant concentration, reduced oxidation efficiency, and potential formation of difficult-to-degrade compounds (Gong, Y., *et al.* 2016; Dong, X., *et al.* 2015b). Gandon (Gandon-Ros, G., 2021a) found that treating PCB with supercritical water increased the debromination rate from 14.8% to 42.5% when the reaction time was extended from 60 to 120 minutes at 250°C and 20 MPa, but further extension to 180 minutes did not significantly change the rate.

4.4. Analysis of influencing factors

To further investigate the influence of various factors on the bromine removal rate, this review analyzed the impact of temperature, pressure, and reaction time using the Pearson correlation coefficient method.

4.4.1. Methods of analysis

The fluids identified for analysis included methanol, isopropyl alcohol, propyl alcohol, carbon dioxide, and water. The removal targets were tetrabromodiphenyl A and BFRs, commonly used in flame retardancy for plastic polymers and printed circuit boards (Wu, H., *et al.* 2021). A total of 108 datasets were analyzed, based on Wang's (Wang, Y., & Zhang, F. 2012a) treatment of TBBPA with different fluids, resulting in 70 datasets under varying temperatures and pressures, and Gandon-Ros's (Gandon-Ros, G., *et al.* 2021b) data using supercritical water at different temperatures and pressures. The data in this section are presented in table S1 of the appendix.

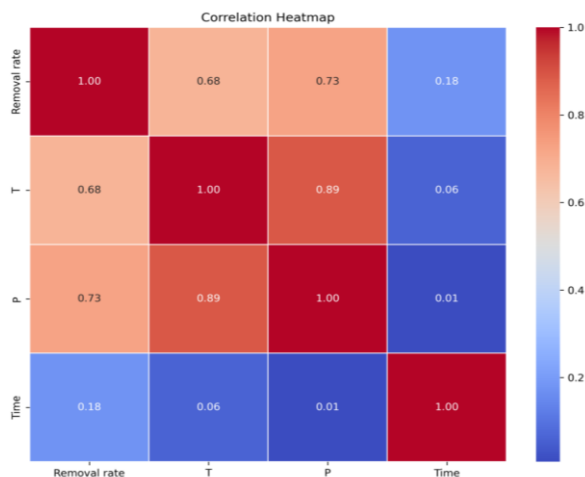


Figure 7. Plot of correlation coefficients between reaction time, temperature and pressure

4.4.2. Analysis of results and discussion

4.4.2.1 Analysis of results

The graph indicates that pressure has a stronger correlation with the reaction outcome compared to reaction time and temperature, suggesting that pressure is the most significant factor influencing the process. This observation can be explained by two key factors:

Firstly, higher pressure accelerates oxidation extraction by enhancing fluid solubility and maximizing the dissolution of substances. Increased pressure also improves fluid diffusion capacity and mass transfer coefficients, optimizing the extraction of target compounds.

Secondly, according to Le Chatelier's principle, increasing pressure in oxidation reactions shifts the equilibrium toward the side with fewer gaseous substances, altering the reaction's equilibrium position. Enhanced pressure also increases the solubility and diffusion rate of oxygen, which is critical for many reactions. This improvement in oxygen mass transfer promotes the reaction process.

Data also shows that the addition of a catalyst significantly increases the debromination rate. The impact of catalysts in supercritical fluids (SCFs) can be attributed to three main mechanisms:

Firstly, Enhanced Reaction Activity: In SCFs, catalysts increase reaction activity by improving contact between the catalyst and reactants, thus increasing the likelihood of reaction occurrence. For example, Zhang *et al.* (Zhang, X., *et al.* 2024) demonstrated that adding magnesium ions to supercritical carbon dioxide improved contact between reacting substances, accelerating the reaction.

Secondly, Regulation of Intermediate Products: Catalysts influence the formation and transformation of intermediate products in SCFs. The high diffusivity and mild reaction conditions of SCFs promote the formation of intermediates, with the catalyst playing a crucial role. Bertuol (Bertuol, D. A., *et al.* 2016) showed that supercritical CO₂ with H₂O₂ facilitated the recycling of lithium-ion batteries by promoting the formation of intermediate H⁺ ions.

Thirdly, Regulation of Reaction Medium Properties: Catalysts affect the physical and chemical properties of SCFs, such as density and solubility, which in turn influence reaction kinetics and thermodynamics (Teja & Eckert, 2000).

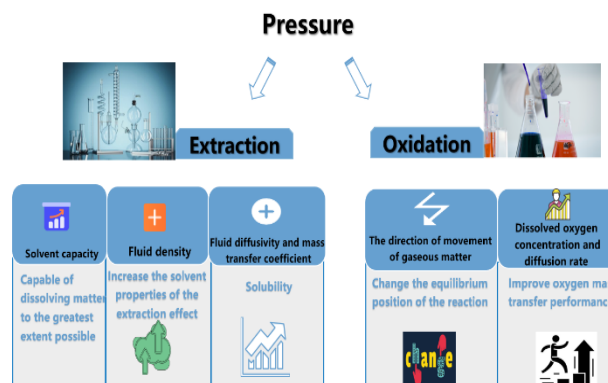


Figure 8. Mechanism diagram of pressure influence

4.4.2.2 Discussion of results

Pressure, being the factor with the greatest degree of influence, affects both typical reactions of the SCF, primarily through the linear variation of both reaction rate and the degree of influence.

1. Linear variation of pressure

In SCF extraction, the influence of pressure on extraction effectiveness is complex and non-linear, affected by factors such as extractant type, sample characteristics, and temperature. While increasing pressure generally improves solubility and density, leading to better extraction efficiency, excessive pressure may cause saturation or diminishing returns.

For oxidation processes in SCFs, pressure effects also exhibit non-linearity, varying with specific conditions and systems. Increased pressure can enhance collision frequency between reactants, accelerating oxidation rates and improving oxygen solubility and diffusion. However, excessively high pressure might reduce oxidation rates by affecting oxygen solubility and diffusion (Li, Y., *et al.* 2024c). Thus, optimizing pressure for practical applications requires careful consideration of various factors (Luo, K., *et al.* 2024).

2. Level of Impact

The impact of pressure on SCF extraction and oxidation processes differs due to distinct reaction mechanisms and material transport processes.

In SCF extraction, pressure primarily affects extractant solubility and extraction efficiency. While higher pressure generally enhances solubility and extraction efficiency, overly high pressure may lead to issues such as reduced selectivity and product purity. Therefore, pressure must be carefully optimized to balance solubility improvements with selectivity and purity (Duan, M., *et al.* 2024).

In SCF oxidation, pressure influences reaction efficiency and selectivity. Increased pressure enhances collision frequency, accelerating oxidation rates, but excessive

pressure may hinder oxygen dissolution and diffusion, reducing reaction rates. Pressure variations can also affect oxidation selectivity and product distribution. Thus, precise pressure control is essential for optimizing both efficiency and selectivity (Heger, K., *et al.* 1980).

The Pearson correlation coefficient analysis reveals that pressure significantly impacts the bromine removal rate, suggesting that adjusting pressure can enhance debromination efficiency. Reaction time has a relatively minor impact, and optimizing it can improve experimental efficiency. However, temperature adjustments should be made cautiously.

3. Optimal fluid types for debromination using scf methods

In the next section, we will analyze the removal rates of PBBS and PCBS using four commonly used fluids: water, methanol, isopropyl alcohol, and acetic acid. These fluids are frequently employed in SCF applications due to their excellent transport, dissolution, and reaction properties, which are crucial for effective removal of contaminants. By comparing the removal rates of tetrabromodiphenol A and PBBS with these fluids, we aim to elucidate the influence of fluid selection on the efficiency of BFR removal.

4.5. Common fluid types

4.5.1. Water

Water under supercritical conditions (critical temperature: 374°C; critical pressure: 218 atm) is ideal for specific extractions and reactions. Its high diffusivity, low viscosity, and adjustable polarity make it suitable for green chemistry and materials science applications.

4.5.2. Methanol

At its critical point (critical temperature: 239°C; critical pressure: 8.09 MPa), methanol's properties between liquid and gas states make it valuable for extraction, reaction, and catalysis. Supercritical methanol offers efficient solubilization, enhanced mass transfer, and versatile reaction environments.

4.5.3. Isopropanol

Supercritical isopropanol, characterized by its critical conditions, serves as a versatile solvent, catalyst carrier, and reaction medium. Its properties, determined experimentally, suit a wide range of chemical processes.

4.5.4. Acetic acid

Supercritical acetic acid (critical temperature: 315°C; critical pressure: 5.77 MPa) offers high solubility, low surface tension, and high diffusivity. These properties enhance its utility in chemical reactions, catalyst carrying, and biomass conversion processes.

4.5.5. Advantages and disadvantages

Table S2 in the appendix summarizes the advantages and disadvantages of the four commonly used fluids to better understand their performance and suitability for different applications.

4.6. Optimal fluid screening

4.6.1. Typical BFRs

Tetrabromobisphenol A (TBBPA) and brominated epoxy resins (BERs) are among the most common BFRs, used widely in various industries. TBBPA is found in plastic polymers and printed wiring boards, while BERs are used in plastics and electronics. Both BFRs are persistent and can bioaccumulate, raising environmental and health concerns (Lu *et al.*, 2015; Birnbaum & Staskal, 2004; Kousaiti *et al.*, 2020; Liu *et al.*, 2016; Berger *et al.*, 2003; Di Carlo *et al.*, 1978; Olasunkanmi *et al.*, 2023).

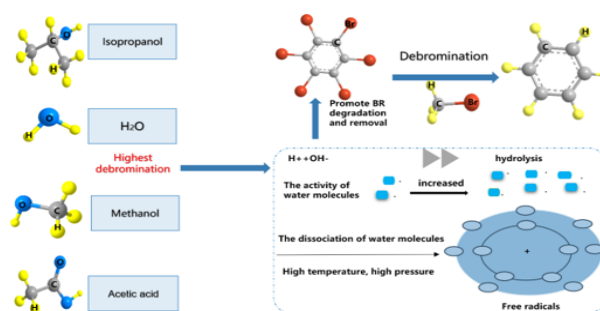


Figure 9. Four fluids to treat two commonly used BFR

TBBPA is mainly used as a reactive BFR in plastic polymers and printed wiring boards (Birnbaum, L. S., & Staskal, D. F. 2004), but also as an additive BFR in a variety of materials such as plastics and rubber (Kousaiti, A., *et al.* 2020).

TBBPA is soluble in aqueous NaOH and slightly soluble in water (Liu, D., *et al.* 2016), and is commonly found in environmental media including water, atmosphere, and in animals. TBBPA can also enter organisms through direct skin contact, inhalation of contaminated air or through the food chain. Berger (Berger, U., *et al.* 2003.) reported the discovery of TBBPA in Norwegian seabird eggs at 13 ng / kg wet weight.

Table 4. Concentrations of TBBPA in various environmental media

Environmental media	Concentration
Kanagawa, Japan	7.7 ~ 130 ng /L (Suzuki, S., & Hasegawa, A. 2006)
Luo Dongjiang, Korea	0.05 ~ 150 ng /g (Lee, I., Kang, H., <i>et al.</i> 2015)
East and South China	up to 4870 ng /L (Zhu, A., <i>et al.</i> 2020).
Liuyang River, China	2.5×10^3 ng/g (Qu, G., <i>et al.</i> 2013).

BERs are produced by incorporating bromine atoms into the epoxy resin molecules, typically through the reaction of a brominating agent with an epoxy compound (Di Carlo,

F. J., *et al.* 1978). These resins generally contain epoxy groups and bromine-substituted structural units. BERs are widely used in the production of plastics and electronics

to reduce their flammability. However, once released into the environment, BERs are highly persistent and can bioaccumulate in living organisms (Olasunkanmi, L. O., *et al.* 2023).

4.6.2. Fluid screening results

The efficiency of various fluids for bromine removal from TBBPA and BFRs follows this order: water > acetic acid > methanol > isopropyl alcohol. Water is the most effective fluid due to its ability to catalyze reactions and enhance bromine removal. The presence of hydrogen ions in water and the production of free radicals at supercritical conditions contribute to its effectiveness.

Firstly, the high debromination rate in aqueous solutions is attributed to the presence of hydrogen ions, which act as effective catalysts for organic reactions. In solutions containing weak acid anions and weak base cations, hydroxide ions from the hydrolysis of weak acid anions react with hydrogen ions from the hydrolysis of weak base cations, forming water and shifting the hydrolytic balance. This promotes mutual hydrolysis and increases the bromine removal rate.

Secondly, the enhanced activity of water under high temperature and pressure conditions is crucial. In supercritical water, increased temperature and pressure enhance the activity, solubility, and reactivity of water molecules. This facilitates reactions between water and bromine atoms in organic compounds, aiding in the removal of bromine.

Thirdly, the polarity and solubility of water are key factors. Supercritical water's high polarity and solubility effectively dissolve organic bromine compounds and stabilize them in the water phase. Increased solubility allows for greater contact between bromine compounds and water, promoting the debromination reaction.

Finally, the generation of free radicals is significant. In supercritical water, the dissociation of water molecules at high temperatures and pressures produces free radicals, such as hydroxyl radicals (OH•) and hydroperoxyl radicals (HO₂•). These highly oxidizing radicals can react with organic bromine compounds, facilitating debromination by breaking down bromine-containing bonds.

Lastly, the role of hydroxyl ions provided by water is extremely important for fluid stability and catalytic performance. According to Liu (Liu, Z., *et al.* 2023) who studied the use of hydroxyl-assisted selective CO electroreduction to formate, the presence of hydroxyl ions leads to the solution possessing four bridging oxygens. The effect of electrode potentials, described using the computational hydrogen electrode model, shows that hydroxyl presence is favorable for the reduction-elimination reaction. Therefore, it can be concluded that hydroxyl groups are likely responsible for the more efficient removal of bromine from water.

5. Conclusions and perspectives

SCF technology is effective for bromine removal and environmental pollution control, offering high efficiency and environmental benefits. The Pearson correlation

coefficient analysis indicates that pressure significantly impacts removal efficiency. Water proves to be the optimal fluid due to its high catalytic activity and effectiveness in debromination. Future research should focus on optimizing SCF process conditions, exploring new SCFs and solvents, understanding bromine removal mechanisms, and developing combined application methods. Advancing these areas will enhance SCF technology's application for BFRs, improving environmental protection and resource utilization.

Despite the effectiveness of SCF technology in removing bromine from BFRs, several challenges remain that require further investigation. Future research should focus on four key areas: optimizing SCF process conditions to improve bromine removal efficiency and selectivity; exploring various SCFs and solvents to identify new, more effective options for bromine removal; investigating the mechanisms of bromine removal to gain a comprehensive understanding of the extraction and oxidation processes and their influencing factors, thus providing theoretical support for technical improvements and industrial applications; and developing combined application methods to enhance both the efficiency and environmental sustainability of bromine removal from BFRs.

Ongoing research and development in these areas will broaden the application prospects of SCF technology for BFRs, significantly advancing environmental protection and resource utilization.

Data availability statement

Data will be made available on request

Conflicts of interest

The authors declare no conflict of interest.

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Author contributions

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Appendix

The appendix contains Tables S1-S2, which providing content that will aid in the research. Table S1 shows the data used for the Pearson correlation coefficient method, and Table S2 presents a comparison of the advantages and disadvantages of the four common fluids and the scenarios in which they are applicable.

Table S1. Selected data

Processed Substance	Fluids	Time /min	Temperature /°C	Pressure /MPa	Removal rate/%	Reference
TBBPA	Methanol	60	400	19	69.2	(Wang, Y., & Zhang, F. 2012b)
	Methanol	60	300	11	22.0	
	Methanol	60	350	16	27.1	
	Methanol	60	400	21	62.7	
	Methanol	60	420	23	67.0	
	Isopropanol	60	400	16	63.6	
	Isopropanol	60	300	6	12.3	
	Isopropanol	60	350	11	33.7	
	Isopropanol	60	400	18	71.3	
	Isopropanol	60	420	22	65.0	
	Water	60	400	19	97.6	
	Water	60	300	5	7.0	
	Water	60	350	12	18.7	
	Water	60	400	21	76.0	
	Water	60	420	23	79.3	
	CO ₂	60	200	1.5	1.4	
	CO ₂	60	250	2.5	80.8	
	CO ₂	60	300	3.5	89.4	
	CO ₂	60	350	1.5	96.1	
	CO ₂	60	375	2	96.9	
	Water	60	200	7	6.5	(Wang, Y., & Zhang, F. 2012c)
	Water	60	250	10	14.8	
	Water	60	300	15	41.3	
	Water	60	350	15	65.9	
	Water	60	400	15	75.8	
	Water	20	170	1	5.6	
	Water	20	180	1	7.2	
	Water	20	190	2	41.3	
	Water	20	200	2	22.8	
	Water	20	220	3	52.3	
	Water	20	240	4	74.9	
	Water	20	260	5	88.4	
	Water	20	280	6	93.8	
	Water	20	300	6	85.60	
	Water	25	170	1	8.1	
	Water	25	180	1	13.6	
	Water	25	190	2	46.4	
	Water	25	200	2	23.6	
	Water	25	220	3	56.5	
	Water	25	240	4	70.8	
Water	25	260	5	84.5		
Water	25	280	6	88.6		
Water	25	300	6	92.1		
Water-methylamine	30	170	1	4.8	Sakabe, J., <i>et al.</i> 2020	
Water-methylamine	30	180	1	15.6		
Water-methylamine	30	190	2	41.2		
Water-methylamine	30	200	2	32.3		

Water-methylamine	30	220	3	58.6		
Water-methylamine	30	240	4	73.6		
Water-methylamine	30	260	5	85.6		
Water-methylamine	30	280	6	82.3		
Water-methylamine	30	300	6	86.8		
Water-methylamine	60	180	1	29.5		
Water-methylamine	60	190	2	44.6		
Water-methylamine	60	220	3	72.6		
Water-methylamine	60	240	4	77.3		
Water-methylamine	60	260	5	90.6		
Water-methylamine	60	300	6	94.8		
Water-methylamine	90	180	1	33.2		
Water-methylamine	90	190	2	54.2		
Water-methylamine	90	220	3	71.9		
Water-methylamine	90	240	4	83.5		
Water-methylamine	90	260	5	88.9		
Water-methylamine	90	280	6	90.2		
Water-methylamine	90	300	6	94.2		
Water-methylamine	120	180	1	34.9		
Water-methylamine	120	190	2	73.5		
Water-methylamine	120	220	3	55.4		
Water-methylamine	120	240	4	84.5		
Water-methylamine	120	260	5	89.5		
Water-methylamine	120	280	6	91.2		
Water-methylamine	120	300	6	94.8		
Methanol	60	180	1	6.40		Uddin, M. A., & Bhaskar, T., Kusaba, T., Hamano, K., <i>et al.</i> 2003
Methanol	60	190	2	15.6		
Methanol	60	200	2	40.4		
Methanol	60	210	2	49.9		
Isopropanol	60	220	3	98.1		
Isopropanol	60	230	3	98.4		
Isopropanol	60	200	1.5	1.4		
Isopropanol	60	250	2.5	80.8		
Water	120	200	2	0	Gandon-Ros, G., <i>et</i>	

Water	120	250	5	40.2	<i>al.</i> 2021c.
Water	120	300	10	76.6	
Water	120	350	18	93.4	
Water	120	400	30	98.5	
Water	60	225	20	19.6	
Water	60	250	20	14.8	
Water	60	275	20	22.4	
Water	120	225	20	29.8	
Water	120	250	20	23.8	
Water	120	275	20	58.4	
Water	180	225	20	37.9	
Water	180	250	20	39.2	
Water	180	275	20	86.8	
Water	240	225	20	38.7	
Water	240	250	20	42.5	
Water	240	275	20	91.7	
Acetic acid	60	180	1.2	6.4	Xing, M., <i>et al.</i> 2020; Xiu, F., <i>et al.</i> 2020
Acetic acid	60	190	1.6	15.6	
Acetic acid	60	200	1.9	40.4	
Acetic acid	60	210	2.3	49.9	
Acetic acid	60	220	2.6	85.6	
Acetic acid	60	230	3.1	87.5	
Acetic acid	60	240	3.2	89.6	
Acetic acid	60	300	3.5	89.4	
Acetic acid	60	350	1.5	96.1	
Acetic acid	60	375	2	96.9	
Acetic acid	60	375	3	97.3	

Table S2. Summarizes the advantages and disadvantages of the four common fluids to better understand their performance and applicability in different application scenarios

Fluid type	Advantages	Disadvantages	Applicable Scenarios	References
Water	<ol style="list-style-type: none"> 1. High density 2. low Surface Tension: contact solid surfaces and improve efficiency. 3. High diffusivity: accelerating the reaction rate. 4. Non-polar solvent properties: properties close to non-polar solvents. 	<ol style="list-style-type: none"> 1. High-pressure and temperature. 2. Solubility limitations: not suitable for all compounds. 3. Product stability: affecting selectivity and product purity. 4. Energy consumption: Large amounts of energy are required 	<ol style="list-style-type: none"> 1. Organic waste treatment and resource recovery: supercritical water can oxidize and degrade organic waste. 2. Biomass conversion: promoting the efficient use of biomass resources. 3. Organic synthesis: promote organic synthesis reactions such as esterification and etherification. 	Leusbrock, I., & <i>et al.</i> 2008 Teja, A. S., & Eckert, C. A. 2000
Isopropanol	<ol style="list-style-type: none"> 1. High solubility: dissolve numerous substances. 2. Unique reactivity: differ from that of ordinary methanol, including reaction pathways and product selectivity. 3. Environmental friendliness: friendly solvent. 4. Process Advantages: Reaction and separation processes possess fast reaction rates. 	<ol style="list-style-type: none"> 1. Toxicity: great toxic. 2. Solubility limitations: usually poorly soluble. 3. High Pressure, High Temperature Conditions: increasing equipment costs and energy consumption. 	<ol style="list-style-type: none"> 1. Chemical synthesis applications: can be used as a solvent or reducing agent, e.g. in metal-catalyzed reactions with bromine compounds to produce hydrogen bromide gas. 2. Energy product preparation: Supercritical methanol can be used as a reaction medium for the production of energy products such as hydrogen, methane and carbon monoxide. 3. Environmental protection: can be used to treat pollutants and toxic wastes, such as organic solvents, heavy metal wastes, etc., and convert them into harmless products. 	Farobie, O., & Matsumura, Y. 2017
Isopropanol	<ol style="list-style-type: none"> 1. Environmentally friendly: no organic solvent residue. 	<ol style="list-style-type: none"> 1. High equipment cost, Strict operation. 	<ol style="list-style-type: none"> 1. Biomass conversion: can be used for biomass conversion, such as 	Fu, B., <i>et al.</i> 2023

	<p>2. Mild reaction conditions: protect the structure of reactants and reduce side reactions.</p> <p>3. Selectivity control can be realized.</p>	<p>2. Energy consumption: consumes a lot of energy.</p> <p>3. Solubility selectivity: poor selectivity with other components.</p>	<p>converting wood fiber, straw, etc. into biofuel or high value-added chemicals, promoting the effective use of biomass resources.</p> <p>2. Material treatment: Supercritical isopropanol can be used for material treatment and modification, utilizing its solubility and reactivity to treat nanomaterials, polymers, etc. under high temperature and high pressure to change their properties and structures.</p> <p>3. Separation technology: The solubility and selectivity of supercritical isopropanol can help to separate and purify target substances such as chemicals and drugs, and is used to separate extracts or purify drug components in drug preparation.</p>	
Acetic acid	<p>1. High solubility: dissolve many substances.</p> <p>2. Adjustability: the solubility and chemical properties can be adjusted.</p> <p>3. Environmentally friendly: no organic solvent residue.</p> <p>4. Fast reaction rate: accelerate the reaction rate and improve the reaction efficiency.</p>	<p>1. High equipment cost: high pressure and high temperature resistant materials, high cost.</p> <p>2. Strict operation requirements: need to strictly control the reaction.</p> <p>3. Energy Consumption: will consume a lot of electricity and fuel.</p> <p>4. Solubility selectivity: poor selectivity with other components, affecting product purity.</p>	<p>1. The use of acetic acid: it can be used as a reaction solvent or extraction agent, such as nucleophilic substitution reaction with bromine compounds, replacing bromine atoms with other functional groups to achieve the purpose of debromination.</p> <p>2. Organic synthesis: supercritical acetic acid can be used as reaction medium or solvent to promote organic esterification, etherification, deoxygenation and other reactions, and to provide a new reaction environment and conditions at high temperature and high pressure.</p> <p>3. Separation technology: the solubility and selectivity of supercritical acetic acid helps to separate and purify chemicals, drugs and other target substances, and is used to separate extracts or purify drug components in drug preparation.</p>	<p>Mylapilli, S. P., & Reddy, S. N. 2020</p>