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1 **On-Line Study of Flame Retardants Extraction in Supercritical CO<sub>2</sub>**

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11 **ABSTRACT**

12 Extraction of brominated flame retardants (BFRs) from polymers before disposal or recycling will alleviate  
13 negative environmental effects and ensure safe usage of recycled products. Supercritical CO<sub>2</sub> is appealing as  
14 solvent owing to its green properties but also challenging due to its limited solvation power towards polar  
15 molecules. For a more comprehensive evaluation of supercritical extraction potentialities, we (i) developed an  
16 on-line analytical technique compatible with both UV-vis and FTIR spectroscopies to enable kinetic and  
17 thermodynamic studies; (ii) studied kinetic extraction of three conventional and two novel BFRs. Concentration  
18 at saturation were determined by gravimetric method or X-ray fluorescence. When compared to UV-vis, FTIR  
19 exhibited a higher applicability to follow BFR extraction's time-dependency binary and ternary systems. Faster  
20 stirring speed, higher temperature, and finer particle size were found to accelerate overall extraction kinetics. In

21 binary systems, times required to achieve equilibrium for each BFR were less than 2 hours at 60 °C, 25 MPa and  
22 1000 rpm. In ternary systems with the presence of cosolvent (water) or polymeric matrix, extraction kinetics  
23 were found to slow down due to competitive dissolution and molecular diffusion within matrix. Mathematical  
24 models derived from irreversible desorption and Fick's diffusion laws were applied to fit observed extraction  
25 kinetics of BFRs with absolute average relative deviations lower than 5.7%, enabling us to identify the rate-  
26 determining step. Our high solubilization rate coefficients measurements for BFRs proves that it can compensate  
27 for their low solubility if one uses flowing supercritical CO<sub>2</sub>.

28 *Keywords:* Extraction; Kinetic; Brominated Flame Retardant; Spectroscopy; Supercritical CO<sub>2</sub>; On-line analysis

## 29 **1. Introduction**

30 Rapid development in polymer science over the past 70 years has led to the introduction of a tremendous  
31 amount of polymeric materials into people's daily life ([Alaee, 2003](#)). To ensure safety and compliance with  
32 flammability standards, the use of flame retardants (FRs) in various polymeric products is essential. Among all  
33 kinds of FRs, brominated flame retardants (BFRs) are the most effective because they require the lowest amount  
34 for the highest flame retardancy, thus their global market demand continues to increase substantially ([Birnbaum](#)  
35 [and Staskal, 2004](#); [Bergman et al., 2012](#); [Gramatica et al., 2016](#)). At present, the market is witnessing a gradual  
36 shift in demand for novel BFRs, in part driven by the phasing-out of widely used BFRs such as polybrominated  
37 diphenyl ethers, now regulated by Stockholm Convention due to concerns over risks to public and ecosystem  
38 health ([Bramwell et al., 2017](#); [Stubblings et al., 2019](#)). Apart from more than seventy-five kinds of conventional  
39 BFRs, around sixty kinds of novel BFRs were reported to be used world-wide but also be ubiquitous in the  
40 environment ([Georlette, 2001](#); [Liu et al., 2016](#); [Yu et al., 2016](#); [Zuiderveen et al., 2020](#)). Detailed reviews on  
41 various BFRs have already been reported ([Alaee, 2003](#); [Covaci et al., 2011](#); [Ma et al., 2016](#)).

42           However, the presence of bromine in BFRs leads to many challenges whether on health and safety, due to  
43 their toxicity, or on their proper disposal or recycling. Indeed, the occurrence of most BFRs in various  
44 environmental matrices can cause adverse effects on diverse organisms through different modes of action, such  
45 as hormone disruption and genotoxicity (Kim et al., 2014; Xiong et al., 2019). Incineration has the disadvantage  
46 of generating corrosive or gases and possibly highly toxic dioxins (Sakai et al., 2001; Ni et al., 2012).  
47 Landfilling results in the leaching of toxic brominated substance with the possible transfer into local aquifers,  
48 especially in the case of additive BFRs that are simply blended with polymers (Zhou et al., 2013; Cristale et al.,  
49 2019). Even in mechanically recycled plastics, uncontrolled BFR additives can cause fluctuation in their quality.  
50 Therefore, the removal of BFRs from polymers has been a necessity in order to recycle or even simply dispose  
51 them.

52           Solvent-based extraction has been proposed to remove BFRs from polymeric substrates with organic  
53 solvents, such as toluene, methanol, or glycol ether based compounds (Nakajima et al., 2002; Altwaiq et al.,  
54 2003; Zhang and Zhang, 2012). From the extractions, resulting polymers could be decontaminated and retained  
55 most of their original qualities. Furthermore, solvents could be reused by distillation. Hence, some commercial  
56 processes have been reported, like CreaSolv, which uses a combination of solvents to extract various BFRs  
57 (Freegard et al., 2006). Although the process is effective, the use of organic solvents should be minimized due to  
58 the related health and safety issues (toxicity, flammability, risks associated with distillation). Another drawback  
59 of the traditional solvent extraction is that the subsequent distillation and drying processes are energy-intensive,  
60 leading to increase in operational costs.

61           Supercritical CO<sub>2</sub> (ScCO<sub>2</sub>) presents an attractive advantage over organic solvent for the extraction of  
62 BFRs, mainly because it is cheap, non-toxic and non-flammable by nature, has high mass and thermal  
63 diffusivity, and allows for an easy recovery by simple decompression of solvent-free extracted substances

64 (Taylor, 1996; Beckman, 2004). Solubility or saturated concentration is one of the most important parameters to  
65 determine limits of extractability, thus, solubilities of some conventional BFRs have been measured in ScCO<sub>2</sub> as  
66 function of pressure and temperature (Gamse et al., 2000; Peng et al., 2014). Also, ScCO<sub>2</sub> extraction of BFRs  
67 was proved to be of various degrees of success in extraction efficiency with or without co-solvents, although the  
68 solvation power of ScCO<sub>2</sub> is generally limited towards polar or high molecular weight compounds (Marioth et  
69 al., 1996; Suzuki et al., 2002; Altwaiq et al., 2003). Otherwise, extraction kinetics must be investigated to  
70 validate process scale-up and develop successful industrial processes (Nimet et al., 2011; Sodeifian et al., 2016;  
71 Villanueva-Bermejo et al., 2020). Despite this, to our knowledge, there have only been few such studies reported  
72 previously, either off-line or on-line, for BFR extraction (Bunte et al., 1996; Wang et al., 2004). This study  
73 proposes to evaluate feasibility of BFR extraction using ScCO<sub>2</sub> considering thermodynamic and kinetic point of  
74 view. We therefore report here a method coupling versatile high pressure vessel with both on-line UV-vis and  
75 mid-IR spectrometers and demonstrate their applicability: (i) to perform spectroscopic analysis of multi-  
76 component mixtures such binary and ternary mixtures in ScCO<sub>2</sub> media; and (ii) to investigate effects of  
77 temperature, pressure, stirring, and matrix size on extraction kinetics for five BFRs, including three of the most  
78 used conventional ones and two popular novel ones.

## 79 **2. Materials and methods**

### 80 *2.1 Materials*

81 Five selected BFR compounds: (i) 3,3',5,5'-Tetrabromobisphenol A (TBBPA) and (ii) 1,2,5,6,9,10-  
82 Hexabromocyclododecane (HBCD) were purchased from Sigma-Aldrich (St. Louis, MO, USA); (iii)  
83 Decabromodiphenyl ether (DBDBE) and (iv) 2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ)  
84 were purchased from Macklin (Shanghai, China); (v) 2,2-Bis[3,5-dibromo-4-(2,3-

85 dibromopropoxy)phenyl]propane (TBBPA-BDBPE) was purchased from Aladdin (Shanghai, China). The BFRs'  
86 Chemical structures and other detailed information are presented in Fig. S. 1 and table S. 1, respectively. Since  
87 HBCD and DBDBE have relative lower purities, they were purified in flowing ScCO<sub>2</sub> at 60 °C and 25 MPa for 6 h  
88 (Gamse et al., 2000). The other BFR compounds were used without any further purification.

89 Ultra-pure water was obtained from a water purification system (WaterPro<sup>®</sup>, Labconco Co., USA), with a  
90 resistivity of 18.2 MΩ·cm at 25 °C.

91 Liquid CO<sub>2</sub> was supplied by CryoExpress Pte. Ltd. (Singapore) with a purity of 99.9%.

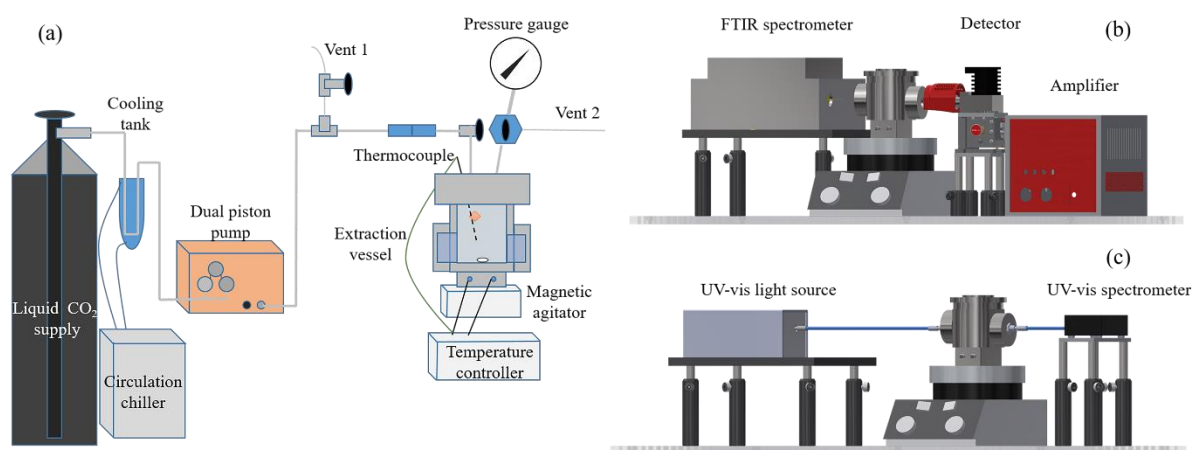
92 Acrylonitrile butadiene styrene (ABS) resin was selected as typical polymer substrate for additive BFRs  
93 because it is commonly used in consumer products, such as housing of electric appliances, electronics, and toys.  
94 BFR-free ABS and BFR-containing ABS pellets were fabricated as industrial practices by Shandong Tianyi  
95 Chemical Co., Ltd. (China) as follows. Industrial grade TBBPA and TBBPA-BDBPE were respectively  
96 incorporated in the BFR-free ABS resin by hot blending with a proportion of 13 wt.% and the resulted mixtures  
97 were extruded to obtain pellets. We then grinded these as-purchased pellets into powders with a centrifugal mill  
98 (ZM 200, Retsch, Germany), at cryogenic temperature using liquid N<sub>2</sub>, then sieved the powders into two particle  
99 size fractions ( $D_{ABS}$ ) in the ranges: (i) 0.25-1 mm, and (ii) less than 0.25 mm.

## 100 2.2 Experimental apparatus

101 A schematic representation of our ScCO<sub>2</sub> extraction system optically coupled with on-line spectrometers  
102 (FTIR and UV-vis) is shown in Fig. 1. The core part of the system, the extraction reactor, is a commercial  
103 pressure vessel from Parr Instrumental Company, USA (ref. 2430HC2), modified as per our requirements with  
104 optical windows to enable spectroscopic studies for operating pressure and temperature ranging up to 35 MPa  
105 and 200 °C. The vessel has an entire volume of 75.4 mL, with minimized dead volumes from filling and venting  
106 ports. Two dismountable windows (made of sapphire for FTIR or fused silica for UV-vis; rupture modulus: 1200

107 MPa versus 100 MPa; diameter: 25 mm; thickness: 15.7 mm) are located on each side of the vessel in  
 108 opposition to each other. Each window is maintained in place thanks to a window holder and sealed by a Teflon  
 109 O-ring and a Teflon cushion through “opposed force” (Fig. S. 2). The resulted optical path length is measured of  
 110 58 mm, sufficiently long to give desired sensitivity and limits of detectability (Jackson et al., 1995; Poliakoff et  
 111 al., 1995).

112 For the other parts of the ScCO<sub>2</sub> extraction system (Fig. 1a), liquid CO<sub>2</sub> coming from a liquid tank is first  
 113 cooled by a circulation chiller (F250, Julabo, Germany) prior to its delivery to a pressure dual piston pump (LD-  
 114 Class, Teledyne ISCO, USA). The vessel temperature is monitored using a K-type thermocouple inserted into a  
 115 stainless steel plunger. Two PID controlled (E5CC, Omron, Japan) electric cartridge heaters, slid into cavities in  
 116 the bottom of the vessel, are used to raise the vessel’s temperature. A magnetic agitator (MR 3001 K, Heidolph,  
 117 Germany) drives a 12 × 3 mm Teflon-coated stirring bar to stir the contents in the vessel. Additional accessories  
 118 permit measurements of pressure, temperature, and agitation speed with a precision of 0.1 MPa, 0.1°C, and 3%,  
 119 respectively.



120  
 121 **Fig. 1.** Schematic illustration of the experimental ScCO<sub>2</sub> extraction system (a), where each component of the system is not  
 122 presented in proportion; the virtual deployment of the vessel with FTIR (b) and with UV-vis spectroscopic components (c),  
 123 and the vessel head parts (model 4792) and the spilt rings (A455HC) are abridged for clearly presenting their optical

124 alignment.

125 The spectroscopic components are combined with the ScCO<sub>2</sub> extraction system in a modular fashion (Fig.  
126 1b and Fig. 1c). Their optical alignment is readily adjusted thanks to bases and supporting rods purchased from  
127 Thorlabs Inc. (USA). The IR beam provided by a FTIR spectrometer (Bruker Alpha OEM, Bruker Optics Inc.,  
128 Germany) transmits through the vessel, and the signal are detected by a Stirling Cycle Cooled detector  
129 connected with an amplifier (K508-MCT1000, Infrared Associates, U.S.A). They were initially integrated as an  
130 on-line monitoring of microfluidic processes (C. Penisson, 2018; Kokoric et al., 2018; Maurice et al., 2020) and  
131 have been reconverted here for the purpose of its extraction reactor.

132 For UV-vis monitoring, the UV radiation emanating from a deuterium light source (DH-MINI, Ocean  
133 Optics Inc., UK) transfers through the vessel, a pair of optical fibers, and several collimating lens. Spectra were  
134 recorded by a UV-vis spectrometer (Flame-T, Ocean Optics Inc., UK).

### 135 *2.3 Measurement of extraction kinetics*

136 All BFR extraction experiments in ScCO<sub>2</sub> were carried out using a solid-supercritical fluid extraction  
137 process. Prior to each extraction, a thorough clean-up of the ScCO<sub>2</sub> extraction system was performed with  
138 flowing ScCO<sub>2</sub> until no extra absorbance of contents was detected, and then reference spectra of pure ScCO<sub>2</sub>  
139 were taken using identical operating conditions as sample spectra. To assess reproducibility and improve  
140 precision, each extraction was performed in triplicate. Precisely weighted pure BFR powders (100 mg) or ABS  
141 powders (600 mg) were enclosed within Solidweave mesh (Mesh size=9 μm) folded uniformly like a mailing  
142 envelope, which was then attached inside the vessel at the top of the thermocouple inverted finger, close to the  
143 filling port. After loading the sample, the vessel was hermetically closed and then flushed three times with  
144 gaseous CO<sub>2</sub>. Then it typically took around 10 minutes to heat it and fill it in with compressed CO<sub>2</sub> to the  
145 desired temperature and pressure, prior to stirring at a set speed. Spectra were collected at regular intervals



146 during the whole extraction process. IR spectra were collected with a  $4\text{ cm}^{-1}$  resolution and were obtained by the  
147 Fourier transformation of 64 interferograms. UV spectra were averaged from 1000 scans within an integration  
148 time of 0.015 s. Each extraction experiment was terminated after reaching a steady state where spectra no longer  
149 show any change in absorbance. The decompression procedure was fast (less than 10 s) along with subsequent  
150 refilling with gaseous  $\text{CO}_2$  and no re-deposition of solute back to sample mesh could be observed under a  
151 microscope ( $\times 500$ , RS Pro).

#### 152 *2.4 Determination of saturated concentration*

153 Saturated concentration ( $c_s$ , in mmol/L) is the maximum concentration of a solute dissolved in a solvent.  $c_s$   
154 of individual pure BFR in  $\text{ScCO}_2$  was measured gravimetrically using an analytical balance (MS105, Mettler-  
155 Toledo, USA) with a readability of 0.01 mg and was calculated with the following equation:

$$156 \quad c_s = 10^3 \cdot (m_2 - m_1) / [M_{\text{BFR}} \cdot (V_v - V_s)] \quad (1)$$

157 where  $m_1$  and  $m_2$  indicate the weight of sample package before and after extraction;  $M_{\text{BFR}}$  denotes the molar  
158 mass of the used BFR molecule.  $V_v$  is the vessel volume (75.4 mL) and  $V_s$  is the sample package volume  
159 determined with the water discharging method.

160 Since mass removal of BFR is not measurable gravimetrically for ABS samples, Br content changes of  
161 ABS samples before and after extraction were determined with an X-ray fluorescence analyzer (XRF) (Vanta C,  
162 Olympus, Japan) applying RoHS plus method. For this determination, the powdered ABS samples (200 mg)  
163 were pressed into a circular shaped disc using a hydraulic crimper (MSK-510M, MTI Co., China) at  $160\text{ }^\circ\text{C}$  and  
164 5 MPa for 5 min. The mass removal of BFR can be calculated by dividing Br content of BFR from Br content  
165 difference of the ABS sample, thus the saturated concentration can be calculated with Eq. (1) as well.

166 All experimental data was displayed in a format of mean value  $\pm$  standard deviation.

167 *2.5 IR spectroscopy and data processing*

168 The IR spectra were processed with a software combination of OPUS 7.5 and Python 3.6.8. After baseline  
169 correction, the corresponding absorbance peak of interest ( $A$ ) (Table S. 2) was integrated in the wavenumber  
170 region of  $w_2-w_1$  (in  $\text{cm}^{-1}$ ) using the following equation:

$$171 \quad A = \int_{w_1}^{w_2} \log_{10} \left( \frac{I_0}{I_t} \right) dw \quad (2)$$

172 with  $I_0$  and  $I$  as sample and baseline intensity, respectively.

173 According to Beer-Lambert Law, the integrated absorbance was proportionally converted to BFR  
174 concentration ( $c$ , in  $\text{mmol/L}$ ) in  $\text{ScCO}_2$  (IUPAC, 1997):

$$175 \quad c_t = A_t \cdot c_s / A_s \quad (3)$$

176 where the subscripts t and s indicate timely and saturation readings.

177 Furthermore, the linear sum of the absorbance spectra of each component ( $A_i$ ) was considered for  
178 quantitative interpretation of the overlapped peak area of a mixture ( $A_m$ ):

$$179 \quad A_m = \sum_{i=1}^N A_i \quad (4)$$

180 *2.6 Mathematical modelling of extraction kinetics*

181 In outline, the  $\text{ScCO}_2$  extraction of compounds from solid matrices (porous or not) can be condensed into a  
182 four-step process: (i) diffusion of  $\text{ScCO}_2$  into internal structure of solid matrices; (ii) desorption and solvation of  
183 solute in the  $\text{ScCO}_2$ ; (iii) intra-particle diffusion of the mixture of solute and  $\text{ScCO}_2$  to solid interface; and (iv)  
184 diffusion of the mixture from the solid interface to bulk  $\text{ScCO}_2$  (Madras et al., 1994; Sunarso and Ismadji, 2009;  
185 Huang et al., 2012). All these steps are diffusion limiting steps except for the solubilization step (ii).

186 To achieve specific description of extraction kinetics involving complex phenomena with mathematical  
187 models, we introduced two simplified scenarios, including absence of matrix and well stirred reactor, based on  
188 the assumption that the diffusion steps can be controlled by changing of matrix properties or stirring speed, and

189 hence basic physicochemical models could be applied (Srinivasan et al., 1990). For the solubilization step, an  
 190 irreversible and first order model (linear desorption) was applied to calculate solubilization rate coefficient ( $k_s$ , in  
 191  $h^{-1}$ ) over extraction period ( $t$ , in h) with the following equation (Tan and Liou, 1989; Elektorowicz et al., 2007;  
 192 Jokić et al., 2010):

$$193 \quad \frac{dc}{dt} = k_s(c_s - c_t) \quad (5)$$

194 and with the initial condition:

$$195 \quad t = 0 \text{ h}, c_t = 0 \text{ mmol/L} \quad (6)$$

196 After solving by integration on both sides of the Eq. (5), one can get

$$197 \quad \ln[(c_s - c_t)/c_s] = -k_s \cdot t \quad (7)$$

198 The applied model for the diffusion steps is based on the hot sphere diffusion model derived from Fick's diffusion  
 199 laws assuming that loaded particles consist of solid spheres with uniform radius and initial concentration of  
 200 extracted substance and are immersed into a fluid free from the substance (Crank, 1979; Bartle et al., 1990; Huang  
 201 et al., 2012). The model is expressed as:

$$202 \quad \frac{c_t}{c_s} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp \left[ - \left( \frac{n\pi}{R} \right)^2 D_e t \right] \quad (8)$$

203 with  $D_e$  as effective diffusion coefficient in a solid substrate ( $m^2/h$ ) and  $R$  as radius of spherical solid particles  
 204 (m).

205 For long time, all terms except the first in the series of exponential terms in Eq. (8) become negligible and the  
 206 kinetic curve can be rewritten as:

$$207 \quad \ln[(c_s - c_t)/c_s] = \ln \left( \frac{6}{\pi^2} \right) - \frac{\pi^2 D_e}{R^2} \cdot t \quad (9)$$

208 where  $\pi^2 D_e / R^2$  may also be recast as diffusion rate coefficient  $k_D$  ( $h^{-1}$ ).

209 From Eq. (7) and Eq. (9), a plot of  $\ln[(c_s - c_t)/c_s]$  versus  $t$  may fall onto two intersecting straight lines with  
 210 different slopes  $k_1$  and  $k_2$  (Subra et al., 1998; Hojnik et al., 2008).

211 In addition, absolute average relative deviations (*AARD*, %) between experimental data ( $c_{t,\text{exp}}$ ) and modeled data  
212 ( $c_{t,\text{mod}}$ ) are also evaluated by:

$$213 \quad AARD = \frac{100}{N} \sum_{i=1}^N \frac{|c_{t,\text{exp}} - c_{t,\text{mod}}|}{c_{t,\text{exp}}} \quad (10)$$

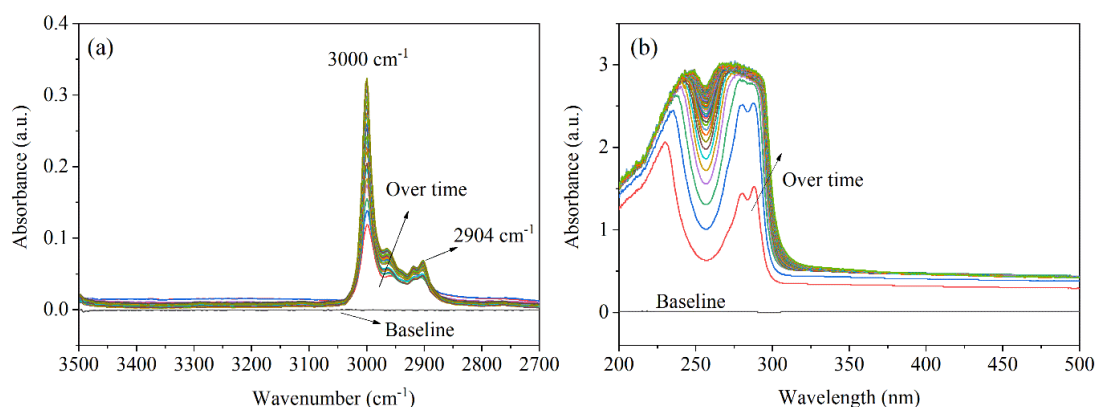
### 214 3. Results and discussion

#### 215 3.1 Comparison between FTIR and UV-vis spectroscopies

216 Spectroscopic monitoring, including vibrational and electronic spectroscopies, is a classical on-line  
217 technique in many supercritical process studies because it allows for rapid and inexpensive determination of  
218 concentration with relatively small amounts of compound (Laintz et al., 1991; Carrott and Wai, 1998; Wang et  
219 al., 2004; Wang et al., 2018). In this study, FTIR and UV-vis spectroscopies were first compared for their  
220 applicability to characterize BFR compounds in ScCO<sub>2</sub>. Raman spectroscopy was not considered since it suffers  
221 from a lack of sensitivity when solute concentrations are low (Jackson et al., 1995). In terms of spectrum  
222 window, the FTIR reference spectrum was narrowed to two available bands of 4500-3880 cm<sup>-1</sup> and of 3500-  
223 2600 cm<sup>-1</sup> (Fig. S. 3a). The other IR bands, including the characteristic C-Br group (690-515 cm<sup>-1</sup>), were  
224 completely obscured by absorptions of sapphire windows and ScCO<sub>2</sub>, itself (Poliakoff et al., 1995). To  
225 circumvent this problem, some identifiable groups, like  $\nu$  (C-H) and  $\nu$  (O-H), were employed to characterize  
226 BFRs in ScCO<sub>2</sub> (Table S. 2). However, due to the ubiquity of these groups in organic chemicals, the high purity  
227 of BFR compounds and the cleanliness of reference spectra are essential to characterize BFRs in ScCO<sub>2</sub>,  
228 especially for a quantitative purpose. Comparatively, the spectrum window of UV-vis could extend to almost the  
229 whole spectrometer's range (200-800 nm) (Fig. S. 3b).

230 With well-defined reference spectra, TBBPA, the most commercially used BFR, was characterized as an  
231 example in ScCO<sub>2</sub> using FTIR and UV-vis spectrometers, respectively (Fig. 2). Both spectra demonstrated

232 incremental absorbance over extraction time until they leveled off and reached a stable value. The FTIR  
233 spectrum of TBBPA was marked by two bands, with two maximum absorbance located at 2904  $\text{cm}^{-1}$  and 3000  
234  $\text{cm}^{-1}$ , resulting from  $\nu$  (C-H alkane) and composite  $\nu$  (C-H combinations) absorption, respectively (Fulton et al.,  
235 1993). In the UV-vis spectrum, TBBPA showed two absorption band (200-260 nm and 260-310 nm) as a result  
236 of electronic transitions,  $\pi \rightarrow \pi^*$  transition (conjugated C=C group), which was similar to the spectrum of  
237 TBBPA through organic solvent presented previously (Lu et al., 1999; Khaled et al., 2018). However, the UV-  
238 vis spectrum of TBBPA exposed an absorbance saturation problem. The high absorptivity of the chromophore in  
239 the UV region set an upper limit of detection, although the issue can be modified by replacing thicker windows  
240 to shorten the optical path length. Besides, a shift of peaks in the UV-vis spectrum was apparent with the  
241 increase of concentration, which resulted in the ambiguous peaks' interpretation.

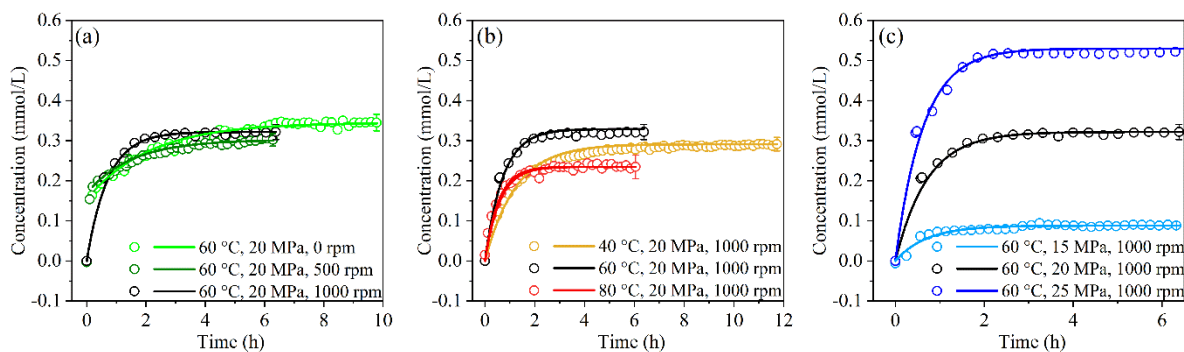


242  
243 **Fig. 2** FTIR (a) and UV-vis (b) spectra of TBBPA in ScCO<sub>2</sub> over extraction period at 60°C, 20 MPa, and 1000 rpm.

244 Although each of the technique has its own advantages and shortcomings from the spectroscopic  
245 standpoint, FTIR is a better technique than UV-Vis for carrying out the on-line monitoring. In addition, the  
246 higher rupture modulus of sapphire than fused silica will facilitate a safer operating condition under high  
247 pressure. Therefore, only FTIR spectroscopy was used in the following sections.

### 248 3.2 Effect of operating conditions

249 To study the influence of operating conditions on extraction performance of BFR in  $\text{ScCO}_2$ , BFR+ $\text{ScCO}_2$   
 250 binary system was first explored based on a simplified scenario in which the matrix was absent and matrix  
 251 related diffusion steps (i) and (iii) might be negligible (see section 2.6). Regarding the binary equilibria of  
 252 TBBPA and  $\text{ScCO}_2$ , the list of operating conditions explored and the fitting parameters are given in Table 1 and  
 253 corresponding kinetic curves are illustrated in Fig. 3. The good agreement of  $c_s$  result of TBBPA at 60 °C, 20  
 254 MPa and 0 rpm with published one (Gamse et al., 2000) allowed to validate our apparatus for  $c_s$  measurement.  
 255 Additionally, all the kinetic curves showed similar trend that the concentration approached its asymptotic value  
 256 gradually after an initial rapid extraction period.



257  
 258 **Fig. 3** Influence of operating conditions on  $\text{ScCO}_2$  extraction kinetics of TBBPA: stirring speed (a), temperature (b), and  
 259 pressure (c), discrete points and lines denote *experimental* and fitted results, respectively.

Table 1 Saturated concentration and kinetic parameters of selected BFRs in binary system.

BFRs	Operating conditions	$c_s$	$k_s$	AARD
		mmol/L	h <sup>-1</sup>	%
TBBPA	40 °C, 20 MPa, 1000 rpm	0.291±0.004	0.81±0.04	3.16
	60 °C, 15 MPa, 1000 rpm	0.088±0.004	1.43±0.19	4.14
	60 °C, 20 MPa, 0 rpm	0.345±0.021	0.48±0.03	2.52
	60 °C, 20 MPa, 500 rpm	0.302±0.016	0.66±0.04	2.28
	60 °C, 20 MPa, 1000 rpm	0.322±0.019	1.40±0.04	1.11
	60 °C, 25 MPa, 1000 rpm	0.531±0.014	1.59±0.08	2.22
	80 °C, 20 MPa, 1000 rpm	0.235±0.007	1.84±0.09	3.70
HBCD	60 °C, 25 MPa, 1000 rpm	0.064±0.004	4.68±1.09	4.22
DBDPE	60 °C, 25 MPa, 1000 rpm	0.004±0.000	N.C.	N.C.
TBBPA-BDBPE	60 °C, 25 MPa, 1000 rpm	0.154±0.002	4.68±0.91	5.70
TTBP-TAZ	60 °C, 25 MPa, 1000 rpm	0.012±0.000	8.10±1.06	3.71

261 N.C. means not calculated.

262 Stirring was found to improve the extraction kinetic and shorten the time required to achieve saturation  
 263 from 6 hours down to 2 hours, when comparing the three cases of non-stirring, 500 rpm, and 1000 rpm (Fig. 3a).  
 264 Only at the highest stirring speed could the overall experimental scatterplots be fitted well with a first order  
 265 kinetic equation (Eq. 5), indicating the external diffusion step is negligible in the well stirred reactor (the second  
 266 simplified scenario, see section 2.6) by fast stirring and leading to a solubilization-dominated process. Whereas,  
 267 external diffusion becomes more significant with less powerful stirring. Since the rapid increase of  
 268 concentration during the initial compression period was owing to the inevitable agitation caused by filling

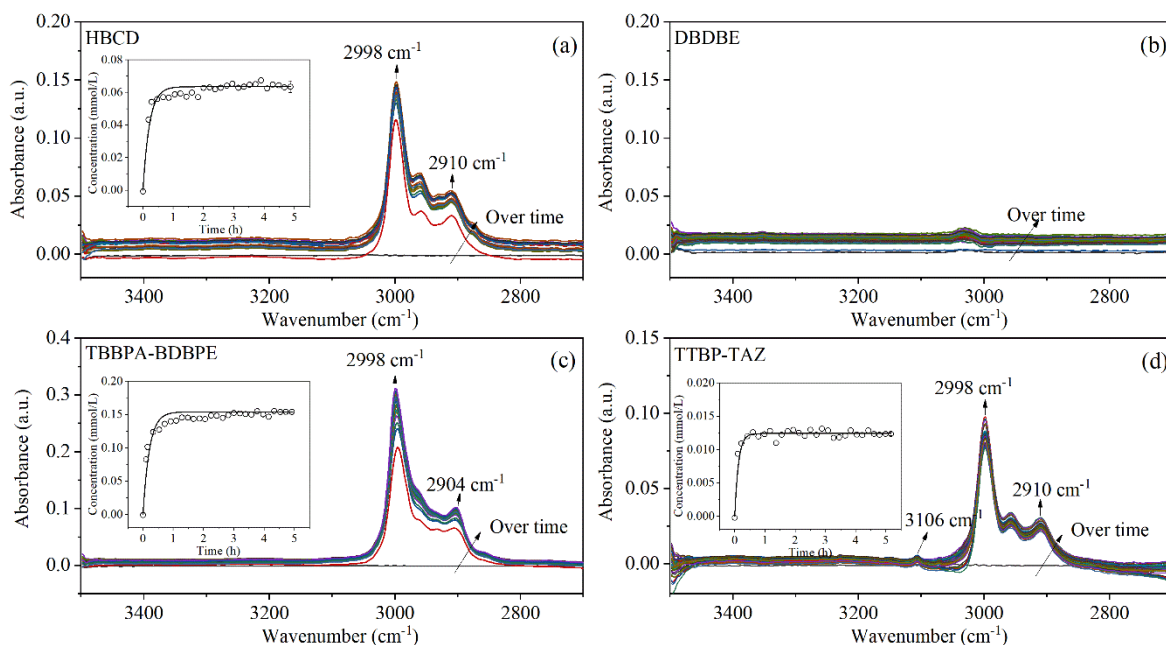
269 turbulences, the fitting model was applied after the initial compression period in the 0 rpm and 500 rpm cases,  
270 where the decreased  $k_s$  can only be attributed to external diffusion. Besides, stirring had insignificant impact on  
271 the solubility of TBBPA considering the measurement's uncertainties of the experiments.

272 The effects of temperature and pressure on extraction of TBBPA were explored at a constant stirring speed  
273 of 1000 rpm (Fig. 3b and Fig. 3c). The  $k_s$  value more than doubled with the increase of temperature from 40 °C  
274 to 80 °C, while the highest  $c_s$  occurred at the intermediate temperature of 60 °C for the studied pressure.  
275 Furthermore, temperature dependent rate coefficients accorded well with Arrhenius equation which states that  
276 the natural logarithm of rate coefficient is proportional to the inverse of absolute temperature (Connors, 1990).  
277 However, we observed that the  $k_s$  value was barely influenced by pressure increased from 15 to 25 MPa at  
278 60 °C, although the solubility was significantly improved. Previous reports have concluded that high  
279 extractability of BFRs in ScCO<sub>2</sub> is generally achieved at high temperature and pressure (Gamse et al., 2000;  
280 Suzuki et al., 2002).

281 Given consideration of both kinetic and thermodynamic aspects, an optimized operating condition (60 °C,  
282 25 MPa, 1000 rpm) was also applied for the other four BFRs. As shown in Fig. 4, each BFR had a fingerprint  
283 spectrum within the band of 3800-2700 cm<sup>-1</sup>, resulting in a kinetic curve except for DBDBE, which does not  
284 contain any identifiable groups in its chemical structure. The specific spectral patterns were also verified by  
285 additional ATR-FTIR characterizations of pure BFR powders (Fig. S. 4). Actually, compared with ATR-FTIR  
286 spectra, the on-line FTIR spectra showed slight difference in a red shift phenomenon due to the formation of  
287 hydrogen bonding in ScCO<sub>2</sub> and in relative absorbance intensity of different groups due to the existence of  
288 ScCO<sub>2</sub> and sapphire windows (Fulton et al., 1993; Poliakoff et al., 1995). Regarding to the extraction  
289 performances of HBCD, TBBPA-BDBPE, and TTBP-TAZ in ScCO<sub>2</sub>, saturated concentrations were lower but  
290 periods required to reach equilibria were all below one hour with comparison to TBBPA. DBDBE had the



291 lowest solubility, hence it was identified as the most difficult BFR to extract (Peng et al., 2014). Overall, high  
292 rate coefficients indicate that a dynamic extraction with fast flowing ScCO<sub>2</sub> could be an efficient process,  
293 because concentration gradient can be kept high enough to drive the extraction in a stationary mode.



294  
295 Fig. 4 FTIR spectra over extraction period and resulted kinetic curves of four BFRs at 60 °C, 25 MPa, and 1000 rpm.

### 296 3.3 Effect of loading water as cosolvent

297 In ternary systems, water was first included as cosolvent along with BFR and ScCO<sub>2</sub> since a small amount  
298 of water added to ScCO<sub>2</sub> was reported to increase the solubility of polar species in nonpolar solvent (Jackson et  
299 al., 1995). Other organic solvents were not included because of their high miscibility in ScCO<sub>2</sub> inducing a large  
300 IR absorbance in the studied band. The FTIR spectra of TBBPA with loading of ultra-pure water (200 μL, below  
301 saturation) were recorded over the extraction period (Fig. S. 5a). The absorbance caused by O-H stretching of  
302 H<sub>2</sub>O molecules did not interfere with the absorbance of TBBPA, thus kinetic curve for both TBBPA and H<sub>2</sub>O  
303 can be followed simultaneously (Fig. S. 5b). Water was faster to reach equilibrium than TBBPA. Despite an  
304 improved *c<sub>s</sub>* of TBBPA by 7% in the presence of such small amount of water, its *k<sub>s</sub>* decreased by 43% probably

305 due to competitive association between TBBPA and H<sub>2</sub>O molecules with ScCO<sub>2</sub> (Table 1 and Table 2). Thus, an  
 306 optimum of extraction performance in the presence of water has to be included in future research. Herein, FTIR  
 307 spectroscopy provides another advantage over UV-vis spectroscopy because water lack spectral transitions in  
 308 the UV region.

309 Table 2 Saturated concentration and kinetic parameters of selected BFRs in ternary systems at 60 °C, 25 MPa, 1000 rpm

BFRs	Cosolvent or matrix effect	$c_s$	$k_s$	$k_D$	$D_e$	AARD
		mmol/L	h <sup>-1</sup>	h <sup>-1</sup>	m <sup>2</sup> /h	%
<b>BFR+H<sub>2</sub>O+ScCO<sub>2</sub></b>						
TBBPA	Loading of 200 μL H <sub>2</sub> O	0.570±0.007	0.91±0.05	N.C.	N.C.	3.59
<b>BFR/ABS+ScCO<sub>2</sub></b>						
TBBPA	$D_{ABS} < 0.25$ mm	0.333±0.001	1.78±0.08	1.08±0.05	$< 1.7 \times 10^{-9}$	2.04
TBBPA	$D_{ABS} 0.25-1$ mm	0.331±0.001	0.49±0.08	0.25±0.02	$4.0 \times 10^{-10}-6.3 \times 10^{-9}$	1.95
TBBPA-BDBPE	$D_{ABS} < 0.25$ mm	0.219±0.004	1.94±0.37	1.32±0.08	$< 2.1 \times 10^{-9}$	2.88

310 N.C. means not calculated.

### 311 3.4 Effect of ABS matrix

312 To discover the matrix effect on extraction performance, BFR-free ABS resin was used as polymeric  
 313 substrate to incorporate with BFRs, including TBBPA and TBBPA-BDBPE. The FTIR spectra of each extraction  
 314 experiment are presented in Fig. S. 6. The extraction of ABS resin itself can also be observed, indicating that  
 315 ScCO<sub>2</sub> has a certain solvation power on ABS, which can increase with temperature and pressure, leading to  
 316 undesired dissolution of polymers or oligomers into ScCO<sub>2</sub> (Sikorski, 1993; Zhao et al., 2018). In the case of  
 317 TBBPA-incorporated samples, the effect of particle size was investigated on their extraction performance, as  
 318 shown in Fig. S. 7. Obviously, the finer particle size, the faster the extraction process. The kinetic curve can be

319 decomposed in two phases, with a first rapid extraction followed by a slower one. Their  $c_s$  of TBBPA were of  
320 similar value, 0.33 mmol/L, lower than that of extraction without ABS matrix (0.53 mmol/L) due to the  
321 competitive dissolution of ABS polymers.

322 According to the broken and intact cell concept, analytes can be distributed at the outer surface of particles  
323 and embedded into their inner structure, just as BFR-incorporated ABS powders after grinding, resulting in  
324 easily accessible BFRs and less accessible BFRs, respectively (Sovová, 1994). Hence, the first rapid extraction  
325 of so-called washing process was controlled by solubilization in the well stirred reactor and  $k_1$  can be assigned to  
326  $k_s$  (Table 2). Furthermore, the sudden reduction of extraction rate after the first part indicates the completion of  
327 accessible BFR's extraction and the intra-particle diffusion resistance came into the effect (Srinivasan et al.,  
328 1990; Alexandrou et al., 1992; Grosso et al., 2010). Hereby,  $k_D$  can be calculated by  $k_D = k_1 - k_2$  and  $D_e$  range can  
329 also be estimated according to Eq. (9). The TBBPA-BDBPE incorporated samples also supported the two-stage  
330 extraction process and the applied models provided very good approximation of experimental data with *AARD*  
331 lower than 2.9%.

#### 332 4. Conclusions

333 In this study, a supercritical reactor was assembled with on-line spectroscopic components to study  $\text{ScCO}_2$   
334 extraction of BFRs. A notable feature of the apparatus, applicable beyond the current study, is the compatibility  
335 with both UV-vis and FTIR spectrometer using the same vessel, enabling to acquire more abundant spectral  
336 information of multi-component mixtures in real time and follow their kinetics. For quantitatively characterizing  
337 BFRs in  $\text{ScCO}_2$ , FTIR spectroscopy is preferable to UV-vis due to its proper detection range and clearer spectral  
338 interpretation despite its limited spectra window. Five BFR molecules were studied using the on-line FTIR  
339 technique along with mathematical modelling. Stirring speed, temperature, and particle size were found to

340 significantly influence extraction kinetics while pressure did not in the considered range. Sufficiently fast  
341 stirring could eliminate limitations due to diffusion of molecules in ScCO<sub>2</sub>, and both higher temperature and  
342 finer grinding size accelerate extraction kinetic. Therefore, high extraction rates could compensate for low  
343 solubility if one applies a dynamic extraction with flowing ScCO<sub>2</sub>. Furthermore, extraction parameters provided  
344 here are valuable to enable a scale-up process design.

345

#### 346 **CRedit authorship contribution statement**

347 **Dong Xia:** Methodology, Investigation, Formal analysis, Writing - original draft. **Ange Maurice:** Software.

348 **Antoine Leybros:** Methodology, Writing - review & editing. **Jong-Min Lee:** Funding acquisition, Resources.

349 **Agnes Grandjean:** Funding acquisition, Formal analysis, Writing - Review & Editing. **Jean-Christophe P.**

350 **Gabriel:** Funding acquisition, Resources, Conceptualization, Methodology, Writing - review & editing,

351 Supervision, Project administration.

352

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