

Deliverable report

Deliverable no./title: D3.3: Purification process using IL/(NA)DES performed with all provided material classes

Lead beneficiary: CTB

Nature of deliverable: Report

Dissemination level: Public (PU)

Due date: 31.07.2021

Grant Agreement number: 820477

Project acronym: CREAToR

Project title: Collection of raw materials, Removal of flAme reTardants and Reuse of secondary raw materials

Funding scheme: H2020-SC5-2018-2019-2020

Coordinator: FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.

Project Website: www.creatorproject.eu

CREATOR CONSORTIUM

PARTICIPANT NUMBER	ABBREVIATION	ORGANISATION
1	ICT	Fraunhofer Gesellschaft für angewandte Forschung – Institut für Chemische Technologie
2	VLB	Volbas S.A.
3	MOS	Machinefabriek Otto Schouten BV
4	CLR	Coolrec BV
5	REL	TREEE – Treatment and Recycling of Electrical & Electronic Equipment
6	GKR	Fundacion Gaiker
7	TCK	Transfercenter für Kunststofftechnik GmbH
8	RMA	Erema Engineering Recycling Maschinen und Anlagen Ges.m.b.H
9	CTB	Centre Scientifique & Technique De L'industrie Textile Belge
10	MAI	Maier S. Coop.
11	DAW	DAW SE
12	CYC	Cyclefibre S.L.
13	CID	Fundacion Cidaut
14	KLU	Kuhne Logistics University GmbH
15	OVM	Openbare Vlaamse Afvalstoffenmaatschappij
16	RWE	RWEnergia Robert Wudarczyk
17	ITB	ITRB Group LTD

DOCUMENT HISTORY AND CONTRIBUTION OF THE PARTNERS

Table 1: Version management

VERSION NR	REVISER	CONTENT
1	CTB	Author of the document
2	ICT	Review
3	CTB	Review
3	Consortium	Approval for publication
4	ICT	Submission

Table 2: Partners' contribution to the deliverable

PARTNER	SHORT NAME	ROLE IN THE WP	CONTRIBUTION TO THE DELIVERABLE
Centexbel	CTB	NADES and scCO ₂ batch extractions	All chapters

ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
APPI	Atmospheric pressure photo ionization
BDE	Bromodiphenylether
BFR	Brominated flame retardants
C&DW	Construction and demolition waste
C&D	Construction and demolition
CDW	Construction and demolition waste
EEE	Electrical and electronic equipment
EoL	End of life
EPS	Expanded polystyrene
GCMS	Gas chromatography- mass spectrometry
HBA	Hydrogen bond acceptor
HBCD	Hexabromocyclododecane
HBD	Hydrogen bond donor
ICP	Inductively coupled plasma
Kt	Kilo tonnes
LC	Liquid chromatography
LIBS	Laser induced breakdown spectroscopy
MS	Mass spectrometry
NADES	Natural Deep Eutectic Solvent
Mt	Million tonnes

PA	Polyamide
PC	Polycarbonate
POP	Persistent organic pollutants
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
REACH	Registration, evaluation, authorisation and restriction of chemicals
Sc-CO ₂	supercritical CO ₂
VOC	Volatile organic compound
WEEE	Waste electrical & electronic equipment
WEEEP	Waste electrical & electronic equipment plastics

TABLE OF CONTENTS

1	INTRODUCTION	7
1.1	MATERIALS AND METHODOLOGIES	8
1.1.1	NADES AND THEIR BUILDING BLOCKS AS EXTRACTION MEDIA	8
1.1.2	C&DW PS FOAM: THE STARTING MATERIAL FOR HBCD EXTRACTION	9
1.1.3	NADES EXTRACTION METHOD	9
1.1.4	SC-CO ₂ EXTRACTION METHOD	9
1.1.5	HBCD CHARACTERIZATION METHODS	10
1.1.5.1	atmospheric pressure photo ionization (APPI)- liquid chromatography (LC) tandem mass spectrometry (MSMS)	10
1.1.5.2	Inductively coupled plasma (ICP)-MS	10
1.2	RESULTS	11
1.2.1	PRELIMINARY STUDIES ON NADES EXTRACTION EFFICIENCY	11
1.2.1.1	Nades screening and selection	11
1.2.1.1.1	APPI-LC/MSMS results	11
1.2.1.1.2	ICP-MS results	14
1.2.1.2	Optimisation of the NADES extraction conditions	14
1.2.2	PRELIMINARY STUDIES ON SC-CO ₂ EXTRACTION	17
2	CONCLUSION	18

1 INTRODUCTION

The EU funded project CREAToR focuses on process development and demonstration (to TRL 5) to remove hazardous, already banned bromine containing flame-retardants from waste streams using continuous purification technologies: supercritical CO₂ and cost-effective solvent-based processes using natural deep eutectic solvents (NADES) in twin-screw extruders.

CREAToR will cover the whole value chain, starting from collecting thermoplastic waste streams from building and construction (B&C) and from waste electrical and electronic equipment (WEEE). The project will implement ways to collect secondary raw materials, identify the presence of hazardous flame retardants, remove these contaminants from the materials and finally reuse the materials.

As case studies they will be reused as valuable secondary raw materials for new B&C insulation panels, closing the circle of economy, for automotive interior application, and for producing 3 D printed parts for aerospace applications. For further increasing the economic feasibility of the approach an optimised logistic concept and a harmonized material quality classification scheme will be developed and applied.

In the CREAToR deliverable "D3.3 Purification process using IL/(NA)DES performed with all provided material classes" the use of Natural Deep Eutectic solvents (NADES) and supercritical CO₂ (sc-CO₂) will be demonstrated as extraction media to remove HBCD fire retardants from a polymer matrix.

The focus of this work is on the removal of the hazardous legacy fire retardant HBCD, which needs to be extracted from a PS foam material used as isolation material in the building sector. Apart from building isolation materials, the HBCD content was also determined in ABS coming from WEEE and fridges, but it was demonstrated that only limited quantities of HBCD were present in these fractions. As a consequence, they could not be used as a reference to optimize the extraction conditions.

At this stage, only HBCD was considered as a flame retardant to be removed from PS. In a next step, it will also be evaluated whether the developed technology would also be applicable for the removal of other bromine-based flame retardants, such as bromodiphenyl ether-based flame retardants (BDE).

Furthermore, PC, PA and PU are also not included in this study, as these materials are only available in limited amounts and therefore less relevant for the current investigation.

All investigations described in this deliverable were performed in a batch-wise manner in order to study the extraction efficiencies. Later on, the results will be used as input for inline extraction experiments and optimizations (as will be described in D3.2 and D3.4).

1.1 MATERIALS AND METHODOLOGIES

1.1.1 NADES AND THEIR BUILDING BLOCKS AS EXTRACTION MEDIA

Centexbel (CTB) is researching the removal of BFR using (natural) deep eutectic solvents or (NA)DES. These are a new class of green solvents with similar characteristics and properties as ionic liquids, but without the inherent toxicity. (NA)DES are synthesized from two or more natural components (solid or liquid), which form a eutectic liquid mixture with a melting temperature lower than the melting temperature of each individual component (Figure 1). The hydrogen bond interactions between the different components are considered to be the driving force behind this eutectic point.

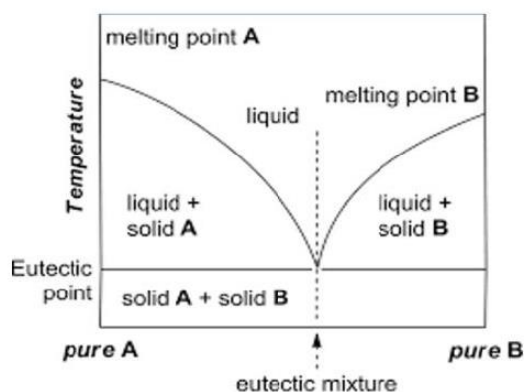


Figure 1: Schematic representation¹ of a eutectic mixture formed from two components.

Most (NA)DES are usually obtained by the complexation of a quaternary ammonium salt (or a halide salt in general) and a hydrogen bond donor, but any combination of a hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) could be a potential (NA)DES. Therefore, the concept of (NA)DES has been extended to also include mixtures of 2 or more organic molecules which attain a eutectic point. However, because some organic molecules have multiple different functional groups (e.g. lactic acid), these substances can function as both a HBA and HBD simultaneously, blurring the lines between a clearly defined HBD and HBA.

Within the CREAToR project, a set of NADES were selected to study their efficiency to extract HBCD from a PS matrix. In this context, both the NADES building blocks and the produced NADES were evaluated as extraction media. The selection was made, based on a literature review, input from suppliers and previous experience, e.g. in the Remadyl project².

¹ Emma L. Smith, A. P. (2014). Deep Eutectic Solvents (DESS) and Their Applications. Chemical reviews, 11060-11082.

² REMADYL, 'a new technique to remove hazardous substances from PVC', a project funded by the Horizon2020 Framework Programme for Research & Innovation G.A.821136 and managed by the EASME, H2020-SC5-2018-2, start date 01/06/2019, duration: 48 months

1.1.2 C&DW PS FOAM: THE STARTING MATERIAL FOR HBCD EXTRACTION

A PS foam material was delivered by DAW, which consisted of white and black foam beads, as shown in figure 2. The material was used as a reference during the further course of optimizations (see section results). A thorough characterization of this starting material was a prerequisite and the HBCD content in the beads was determined to be 1.7%, according to the APPI-LC/MSMS method as described in § 1.1.3.

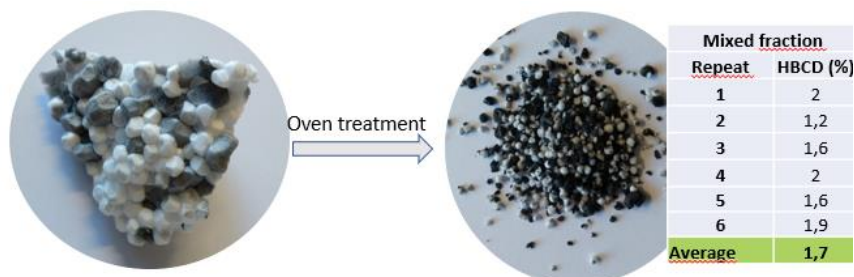


Figure 2: Analysis of the PS reference material. The foam was oventreated and the HBCD content was determined for the mixed and separated black and white fractions.

The HBCD content was also determined by the Transfercenter für Kunststofftechnik GmbH (TCKT) and Fraunhofer Gesellschaft zur Förderung der angewandten Forschung – Institut für Chemische Technologie (ICT) and similar contents were measured, i.e. 1.8 % (as determined by Soxhlet extraction and GCMS) and 1.79 % (via HPLC technique) respectively.

The latter result proves that the three characterization methodologies used in this project give similar results.

1.1.3 NADES EXTRACTION METHOD

In order to evaluate the HBCD extraction efficiencies in NADES, shrunk PS particles were placed in a flat bottom flask, together with the extraction medium (NADES or NADES component). Oven treatment was carried out to reduce the volume of the material, by eliminating the gas present in the beads. After extraction for a certain predefined time, the extracted PS foam and the extraction liquid were separated from each other (see figure 3). Depending on the extraction system used, this was carried out via decanting or filtration, using a paper filter. After isolation of the solid extracted PS material, it was rinsed with an appropriate solvent (water or ethanol) in order to remove residual extraction medium.

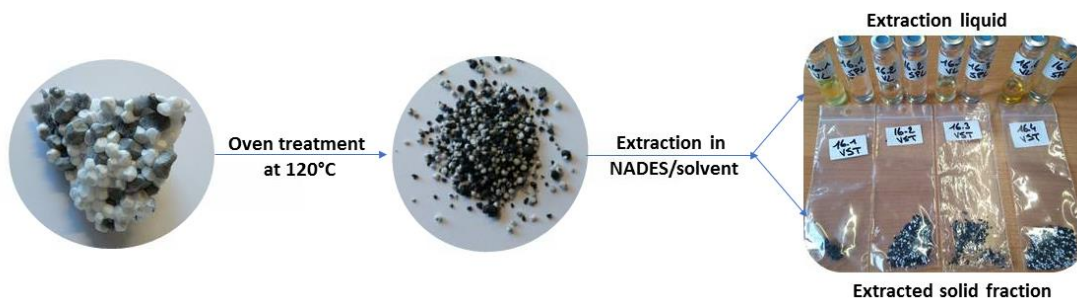


Figure 3: Material flow when performing lab-scale extraction tests

1.1.4 sc-CO₂ EXTRACTION METHOD

To perform sc-CO₂ batch extractions, PS beads were placed in a reaction vessel, which was placed in an oven (see figure 5). Next, the CO₂ flow rate and pressure were adjusted and the vessel with PS material was heated up to the desired temperature. Once a stable process was obtained, the desired co-solvent flow was set. During all conducted experiments, the CO₂ flow was recycled and re-used during the same experiment.

After extraction, the extracted PS was removed from the oven and the co-solvent (if used) from the separator. Figure 4 shows an example of the material flow.

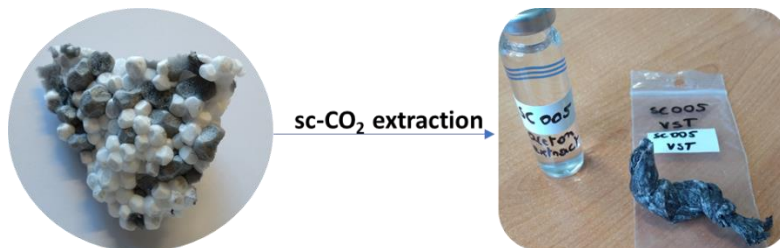


Figure 4: Material flow during a sc-CO₂ extraction experiment

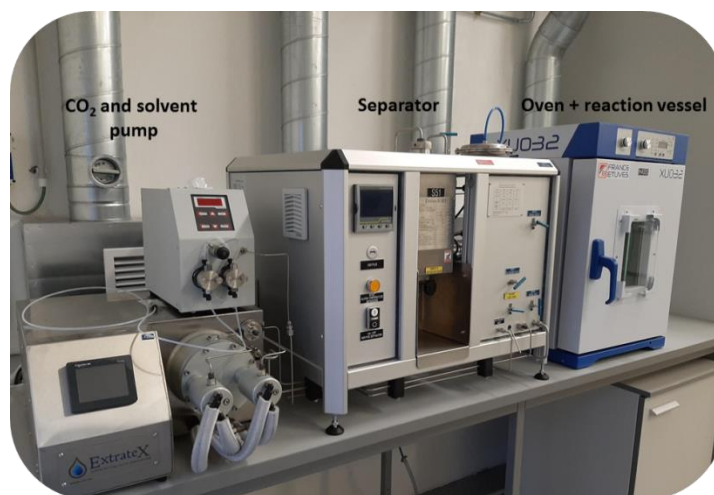


Figure 5: sc-CO₂ reactor, consisting of a CO₂ and co-solvent pump, a reaction vessel placed in an oven and a separator, to split the co-solvent and extracted species from the CO₂.

1.1.5 HBCD CHARACTERIZATION METHODS

1.1.5.1 ATMOSPHERIC PRESSURE PHOTO IONIZATION (APPI)- LIQUID CHROMATOGRAPHY (LC) TANDEM MASS SPECTROMETRY (MSMS)

All solid PS samples and liquid extraction media, which were collected after the extraction experiments, were analyzed via APPI-LC/MSMS. Prior to analysis, the solid samples were extracted with a toluene/methanol mixture, in an ultrasonic bath. By this method, the remaining HBCD amount could be extracted. After extraction, the procedure was repeated once more for each sample. APPI-LC/MSMS analysis was conducted after each extraction step on the extraction media. The samples were injected on an LC column and the components were separated with an appropriate eluents. Detection was established via mass spectrometry (MS/MS operation), using APPI as ionization method. As a result, a chromatogram was obtained, which contains different peaks, representing the different HBCD isomers. Identification and quantification of the peaks was achieved via dedicated software and calibration lines for each isomer (α , β and γ isomers) were determined. A similar methodology was used for the liquid extraction media, but in this case the liquid samples were directly (sometimes after dilution) injected on the LC column.

1.1.5.2 INDUCTIVELY COUPLED PLASMA (ICP)-MS

In the case of the solid PS materials, a second method was evaluated in order to determine the HBCD content, i.e. analysis via ICP-MS. To this end, EN-16711-1(2015) was used as a test standard. In brief, the PS samples were mineralised with concentrated acids in combination with a microwave treatment. In a next step, elemental analysis was performed using ICP-MS to determine the bromine content. It should be emphasised that the absolute values generated via this method deviate from those obtained via LC/MSMS. As a relative comparison technique, both methods are trustworthy.

1.2 RESULTS

1.2.1 PRELIMINARY STUDIES ON NADES EXTRACTION EFFICIENCY

1.2.1.1 NADES SCREENING AND SELECTION

1.2.1.1.1 APPI-LC/MSMS RESULTS

As described in §1.1.4, the oven-treated PS beads were incubated in different NADES solvents or their constituents. Initial extractions were performed for 24 hours, at 100 °C. After extraction, the obtained solid and liquid fractions were analyzed. The figures below show the results obtained via APPI-LC/MSMS for the liquid fractions (figure 6h) and the solid fractions (figure 7).

The graphs display the absolute amount of HBCD which was determined in 0.5 g of PS material (left axis, blue bars), as well as the extraction efficiency (right axis, green dots, as compared to the non-extracted PS foam). Based on the graph in **Fehler! Verweisquelle konnte nicht gefunden werden.**, which focusses on the analysis of the liquid fractions (i.e. the extraction media) the best results can be attributed to the NADES, represented by the highest blue bars (highest amounts of HBCD are detected and thus extracted from PS) and the highest green dots (i.e. the highest amount of HBCD was extracted via the NADES, compared to the amount of HBCD present in the non-extracted PS). In this respect, the best results were obtained when fatty acids were used as extraction solvent e.g. component 2, 3, 7 and 9. Furthermore, the NADES system, consisting of the former two components as well as NADES 7 gave promising results. It should be mentioned that percentages higher than 100 % can be ascribed to the inhomogeneity of the starting material.

Apart from the liquid fractions, the solid PS fractions were also analyzed to quantify the remaining HBCD content after NADES extraction (see graph in figure 7). In this case, the best results are given by component 2, 3, their NADES and component 7, which represent the same fatty acids as mentioned above. Component 5 also showed some promising results.

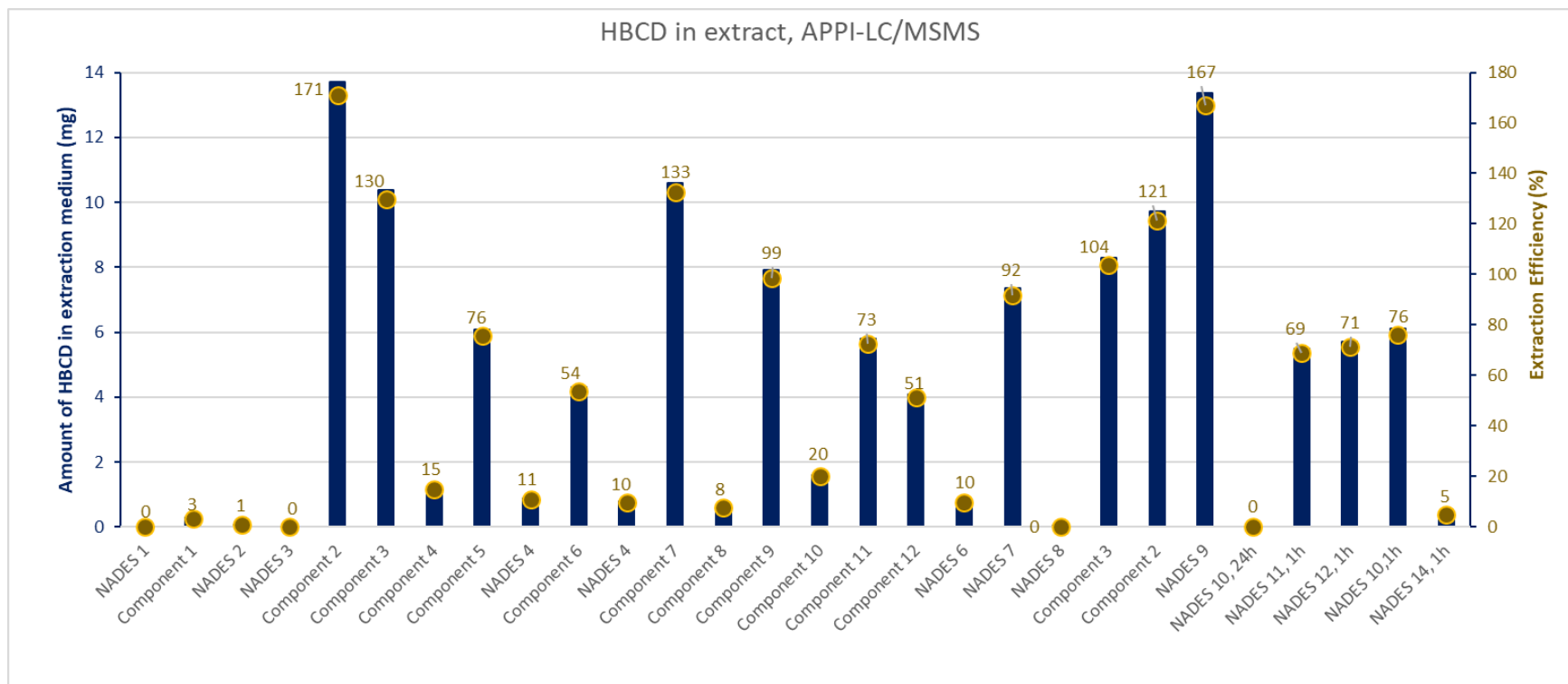


Figure 6: HBCD content (left y-axis) and extraction efficiency (right y-axis), as determined for the liquid fractions, obtained via APPI-LC/MSMS.

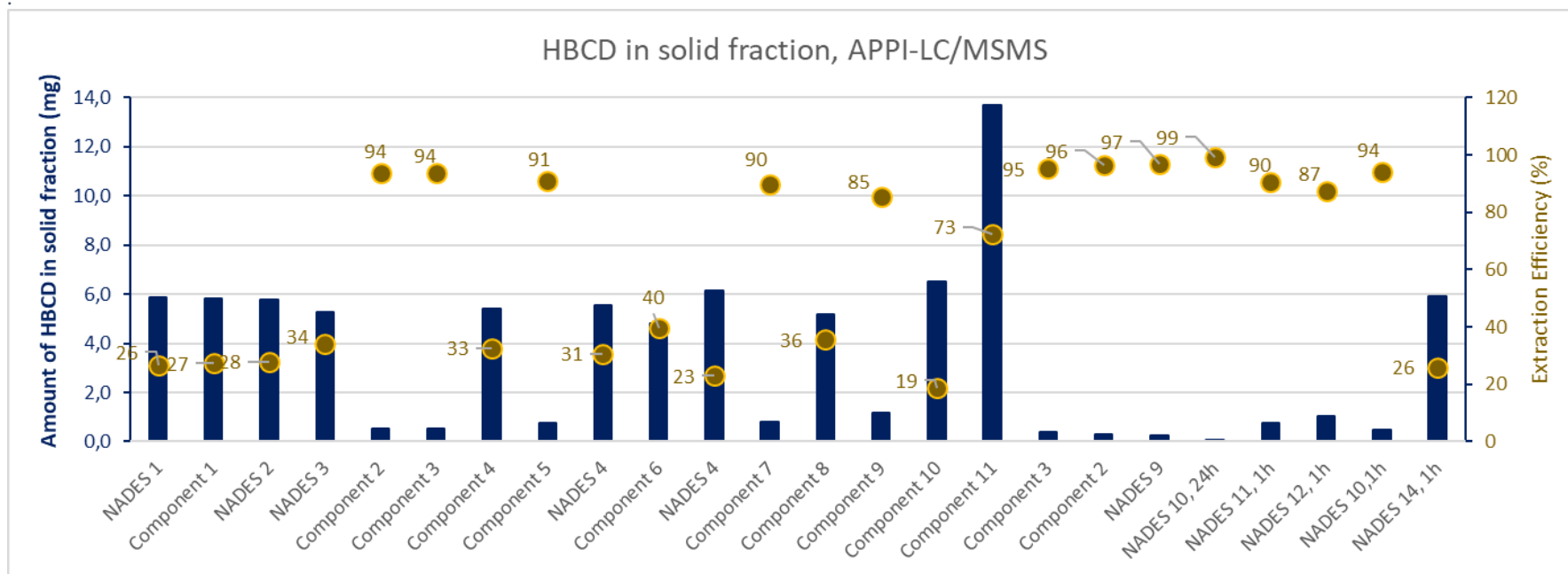


Figure 7: HBCD content (left y-axis) and extraction efficiency (right y-axis) as determined for the solid fractions, obtained via APPI-LC/MSMS.

1.2.1.1.2 ICP-MS RESULTS

A selection of the extracted solid PS fractions was analyzed via ICP-MS. Based on the results in figure 8, it can be stated that ICP-MS offers a valuable alternative to visualize the extraction trends. In this case the bromine content is measured and recalculated to the HBCD content. This also means that if other Br-containing substances are present in the polymer it will not be possible to calculate the HBCD content. In this perspective, it was concluded that APPI-LC/MSMS should be used as the standard analysis technique for future evaluations.

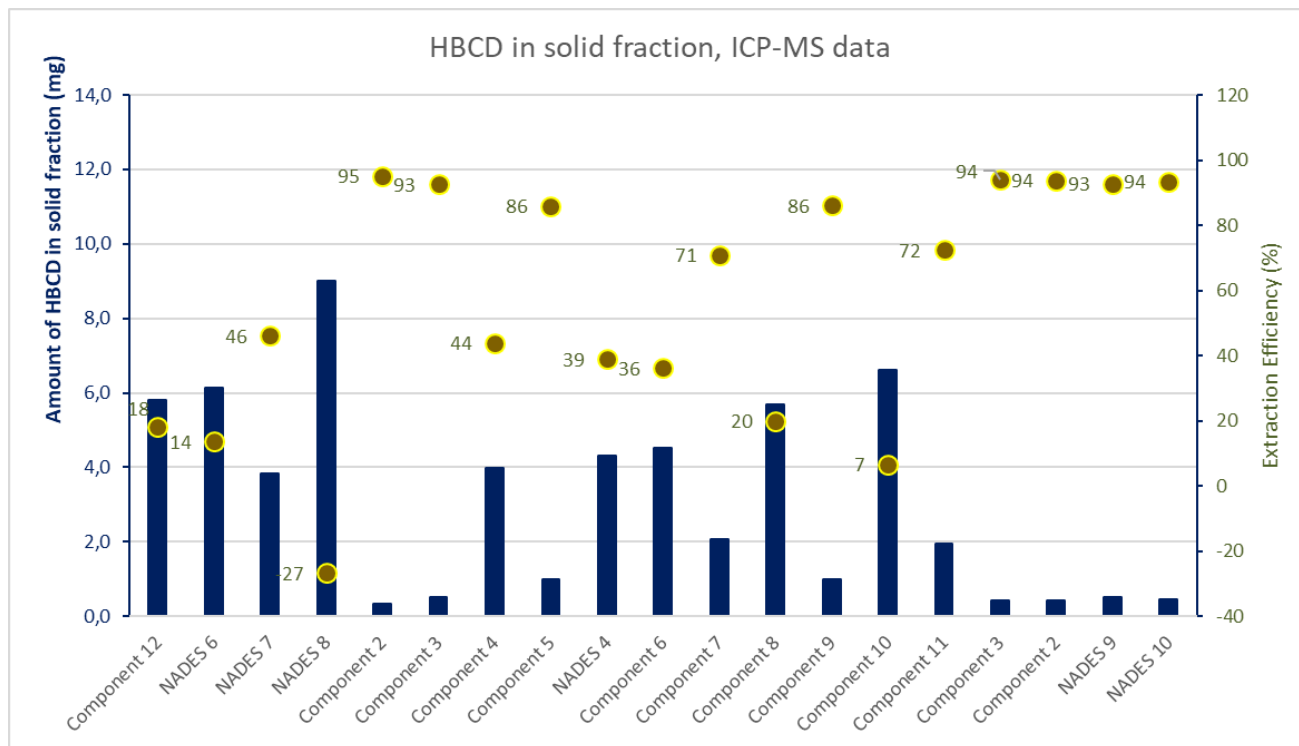


Figure 8: HBCD content, determined for the extracted solid PS fractions, via ICP-MS.

1.2.1.2 OPTIMISATION OF THE NADES EXTRACTION CONDITIONS

Based on the previous results, it was decided to continue with components 2 and 3 to optimize the extraction conditions for these solvents. In this respect, the extraction time and temperature were optimized, and the influence of these parameters on the extraction efficiency was evaluated. Furthermore, their combinations were studied as NADES systems.

Figure 8 shows the percentage of HBCD that was extracted upon adjusting the different parameters. In the case of component 2, extraction efficiencies of 95 % could be reached (at 150 °C) after only 15 minutes. For component 3, 90 % extraction efficiencies were reached after 15 minutes at a temperature of 100 °C.

Apart from the solid fractions, the liquid fractions were also analyzed (i.e. the extraction media). If the total mass of HBCD (i.e. sum of remaining HBCD in the extracted solid fraction + amount of extracted HBCD, present in the liquid fraction) is mapped as a function of the extraction temperature and time (see Figure 99 and Figure 1010), it can be noted that the total mass decreases with increasing temperatures and times. As this finding points in the direction of HBCD degradation, the degradation behavior of HBCD was studied at the different extraction temperatures.

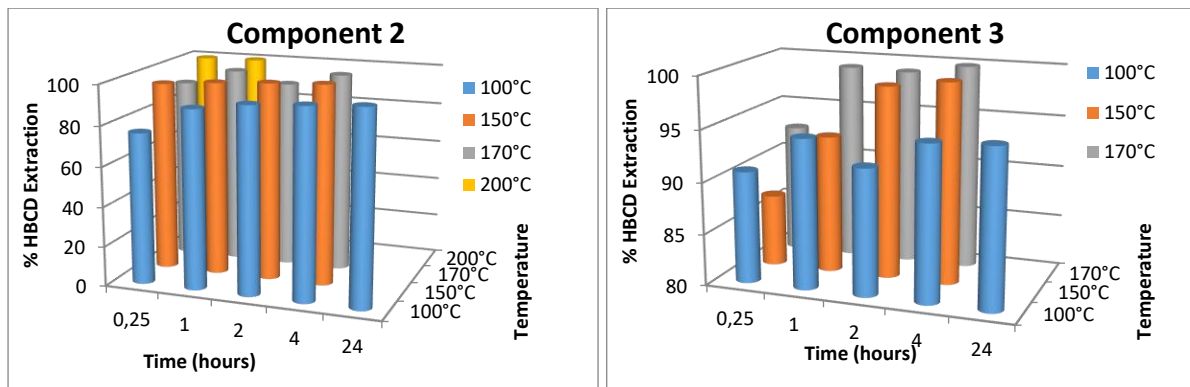


Figure 9: Extraction efficiencies, obtained after extraction with component 2 (left) and component 3 (right), calculated based on the amount of HBCD detected in the extracted solid fraction. Different extraction temperatures and times were evaluated.

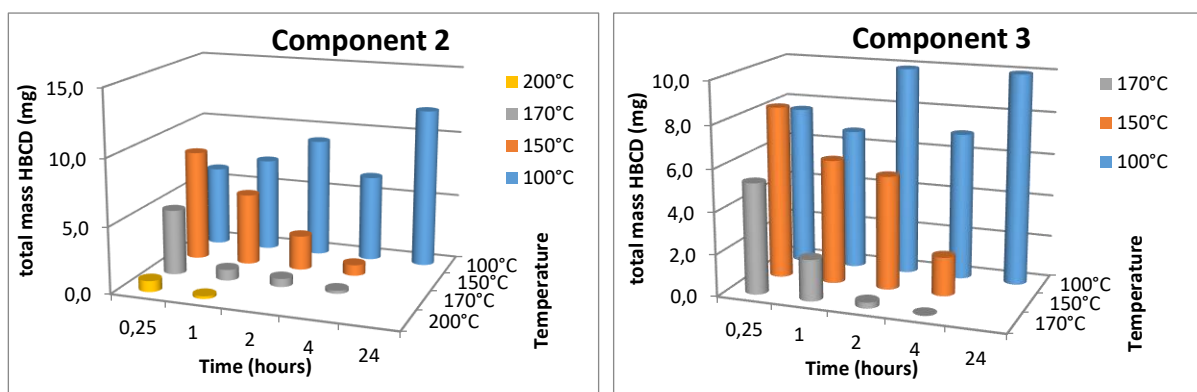


Figure 10: Extraction efficiencies, obtained after extraction with component 2 (left) and component 3 (right). The total mass of HBCD (in liquid + solid fraction) is displayed for both systems, as a function of time and temperature.

To this end, HBCD was heated up to 150, 170 and 200 °C and the degradation was studied by analyzing the volatile organic compounds (VOCs) which were extracted, isolated and analyzed via gas chromatography. The results are shown in figure 11 and explained below.

If HBCD is treated at 150 °C, mainly HBCD isomers are present along with some degradation products (chloroform, a bromo isobutyric acid butylester, 1-bromo, 2-methylpropane, and polyhydroacenaphthene + other cyclic derivatives). Other substances which are present are di-tertbutylether, isobutyric acid and isobutylester. At 170 °C, the chromatogram becomes more pronounced, but no new substances arise. A HBr peak appears only in the beginning of the chromatogram.

At 190 °C, degradation is obvious with a lot of partially debrominated (still cyclic) HBCD products. Furthermore, looking at the volatile VOCs, the amount of HBr is growing. Small brominated degradation products and chloroform have disappeared, but bromocyclohexane and alkyl and alkylbenzenes have appeared. Analysis of the higher VOC and lower VOC region show that lower polycyclic aromatics form the main part of the emission spectrum with also the appearance of a decanoic acid peak. The main polyaromatic compound present is acenaphthene. The other polycyclic compounds are hexahydro acenaphthenes and hexahydrobenzocyclooctenes. Somewhat later a substance like 1,5-cyclododecadien-9-yne, 2,5-dibromo elutes, but also a lot of other unknown small peaks of brominated cyclic and ring opened structures with low bromine content are present.

The increasing volatilisation and degradation may thus explain the deviations in mass balance. These findings should also be considered with regard to safety issues.

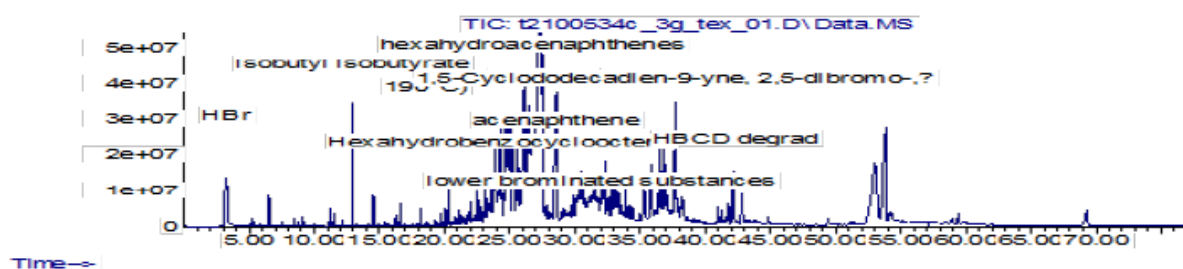
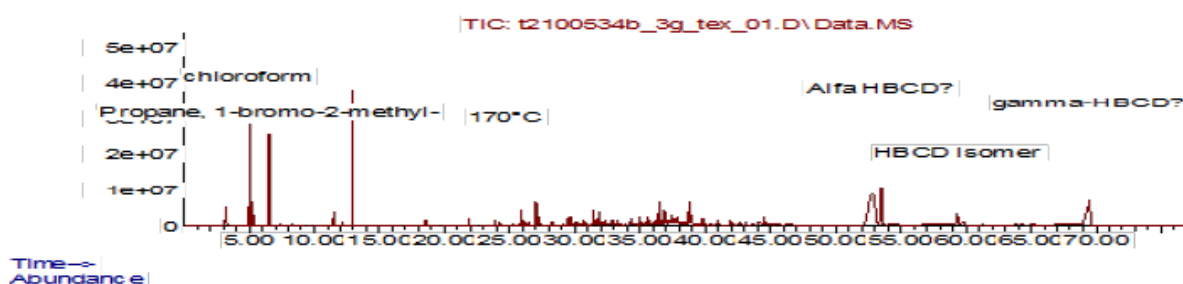
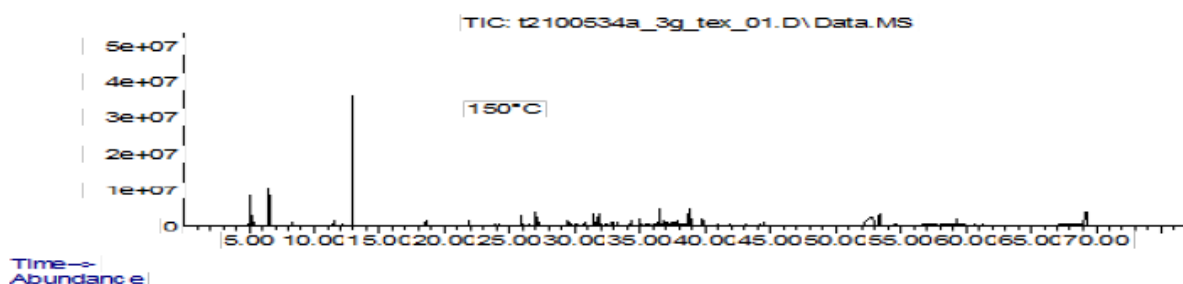
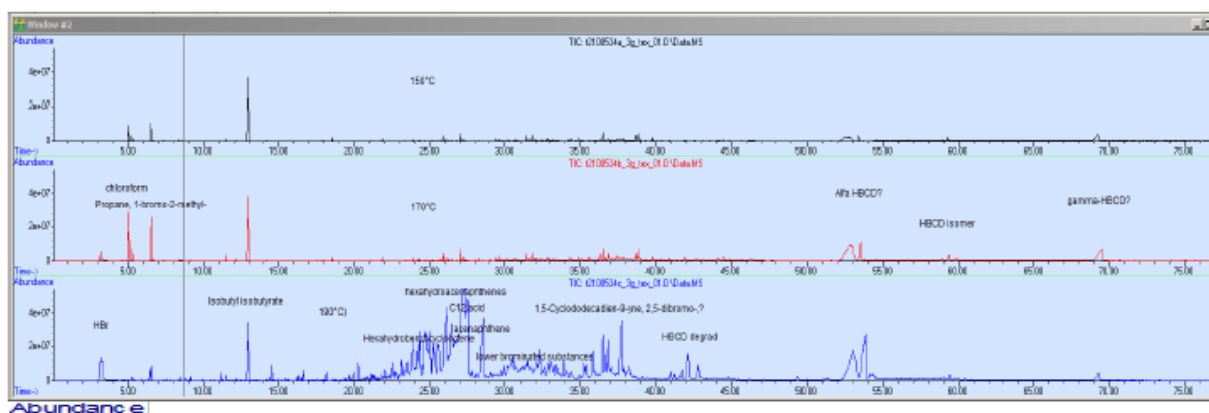


Figure 11: Chromatograms generated for HBCD upon thermal extraction at 150 °C, 170 °C and 190 °C.

For the NADES components 2 and 3, no significant degradation products could be detected upon executing similar thermal extraction experiments at 150, 170 and 190 °C.

1.2.2 PRELIMINARY STUDIES ON SC-CO₂ EXTRACTION

First experiments were conducted with a sc-CO₂ batch reactor, as described in §1.1.4. In a first step, the influence of pressure and temperature on the extraction efficiency was studied. Figure 12 shows how an increased temperature and pressure improve the extraction efficiency. It also seems that the influence of the temperature is more significant than the pressure effect. At 200 °C, a yellow liquid could be collected, which also showed the presence of HBCD after analysis.

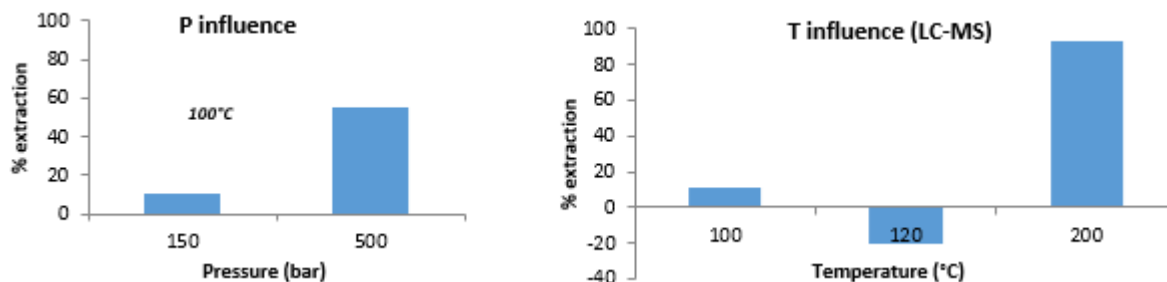


Figure 12: sc-CO₂ batch reactions: influence of pressure and temperature on the HBCD extraction efficiency.

As the pressure during compounding will be fixed at around 150 bar, parameters such as temperature, CO₂ flow, co-solvent flow, but also the influence of the residence time will have to be evaluated. In the case of the latter, for current experiments extraction times of 2-4 hours were used, but inline extractions will limit the extraction time to a maximum of 10 minutes.

In the batch set-up, the influence of co-solvent flow was also studied. To this end, an increasing amount of acetone was added to the process. Figure 13 shows the results obtained. Based on the data, it can be concluded that longer extraction times result in higher extraction efficiencies. Furthermore, in the current set-up, an acetone flow of 0.6 g/min was found as an optimum (at 100°C, 150 bar and 4 hours of extraction).

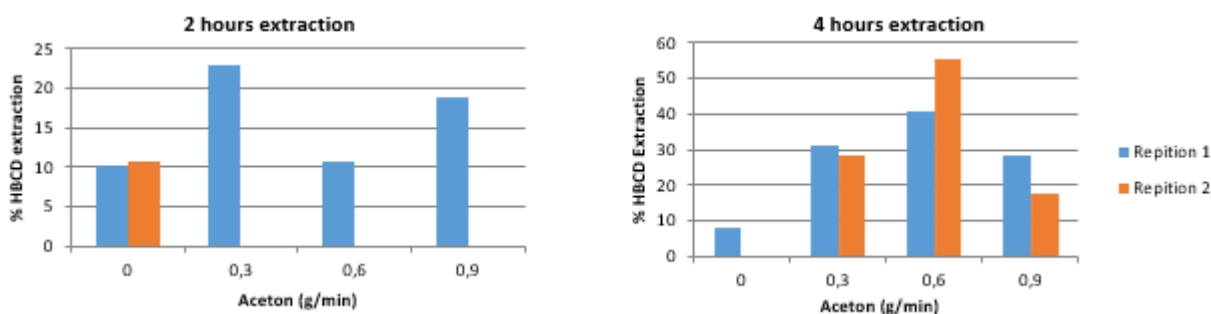


Figure 13: sc-CO₂ batch reactions: influence of co-solvent flow on the HBCD extraction efficiency.

As a preliminary experiment, the influence of NADES addition in the sc-CO₂ batch set-up was also studied. To this end, the insulation foam was placed in the extraction vessel, together with the NADES, at a pressure of 150 bar, a temperature of 100 °C and a CO₂ flow of 10 g/min. An HBCD extraction efficiency of 91 % was obtained. It should be noted that the high yield might be due to the direct contact between the NADES and the insulation material. Inline extraction experiments will have to show the potential of using NADES as a co-solvent.

2 CONCLUSION

In the current deliverable D3.3, the potential of NADES, its constituents and sc-CO₂ (in batch) were studied for their potential as extraction media for the removal of HBCD from PS insulation foam.

It could be demonstrated that the use of fatty acids, such as components 2 and 3 and their combinations, so called NADES, offer great potential as extraction solvents for HBCD. Extraction efficiencies of >90 % could be obtained, even for extraction times of 15 minutes.

It should be kept in mind that increased processing temperatures might initiate HBCD degradation. Especially at temperatures of 170 °C or higher, the degradation products become more apparent.

Next, the extraction of HBCD was demonstrated via sc-CO₂ in a batch reactor, in which higher temperatures are beneficial to maximize extraction. Furthermore, the addition of a co-solvent such as acetone could increase the extraction efficiency.

As a final conclusion, it can be stated that the combination of sc-CO₂ and NADES in an inline operational setting is still worthwhile to investigate. In this respect, first trials with NADES and its components as co-solvents in the inline extrusion set-up are planned in August 2021. The results of these trials and the subsequent steps will be topic of the future deliverable D3.4.