PET Depolymerization to BHET and Purification via Crystallization

Report Monitoring Contamination Levels

Report required by Article 13 of Regulation (EU) 2022/1616

10 October 2023 – updated 16 March 2024

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1. Introduction

The novel technology -*'Polyethylene terephthalate (PET) depolymerization to bis(2-hydroxyethyl)terephthalate (BHET) followed by a series of purification steps of which the main step is crystallization'* was notified as required under Articles 10(2) and 10(3) of Commission Regulation (EU) 2022/1616 on 7 April 2023.

According to Article 13 of Commission Regulation (EU) 2022/1616 *a recycler operating a decontamination installation in accordance with Article 11 of the regulation shall monitor the average contaminant level on the basis of a robust sampling strategy which samples the plastic input batches and the corresponding plastic output batches.* This report summarises the data forthcoming from the monitoring and the information as required by Article 13(5) of the Regulation.

2. Brief description of the novel technology

This novel technology builds on the principle of breaking the polymer matrix to allow more easy access to the contaminants that are usually physically bonded to the polymer and trapped by the matrix. This recycling technology, therefore, counters the difficulties and efficiency limitations often encountered to purify relatively insoluble polymers such as PET when using traditional methods such as extraction and/or partial solubilisation and reprecipitation.

Contrary to mechanical recycling that focuses on the decontamination of the PET polymer, this technology breaks selectively certain chemical bonds of the PET polymer to give a starting molecule - *BHET-* from which the PET polymer can be remade again. The depolymerization is done through glycolysis by heating the PET waste in a reactor in the presence of an excess of ethylene glycol (EG), a monomer which is also used in the manufacturing of PET (Figure 1).
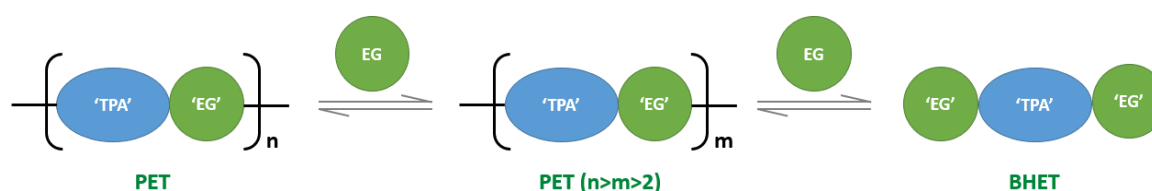
Figure 1. Schematic representation of PET glycolysis; TPA: purified terephthalic acid; EG: ethyleneglycol; BHET: bis(2-hydroxyethyl)terephthalate.

By breaking down the polymer matrix of waste PET, contaminants and additives that are present in the polymer matrix from prior usage of the material are released into the reaction medium; they are no longer physically bound or difficult to access. This allows impurities to be removed in much higher quantities and more efficiently than with mechanical recycling technologies (Figure 2) by standard physical processes like solid/liquid separation, distillation, active substrate adsorption, crystallisation and washing and drying. Therefore, this novel recycling technology can recycle highly contaminated input materials that cannot be recycled by mechanical recycling processes (Welle, 2021).

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Figure 2. Schematic representation of the release of contaminants during glycolysis.

The novel technology can use 3 different waste streams:

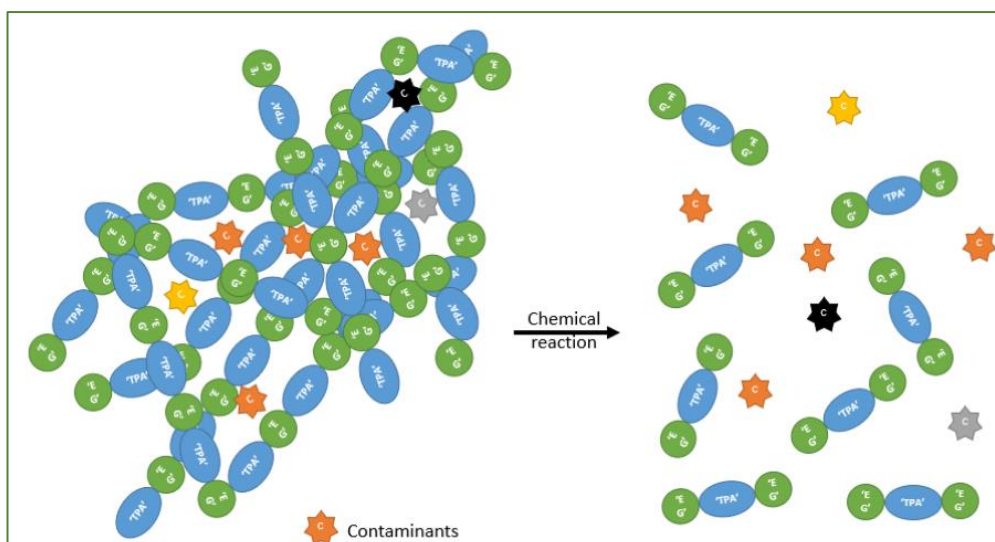- PET waste originating from packaging: Post-consumer and post-industrial PET packaging waste from food and non-food contact applications.
- Post-consumer and post-industrial polyester textile.
- Post-consumer[1] or post-industrial PET film.

These waste streams can deviate from the requirements for collection and pre-processing of Article 6 of Regulation (EU) 2022/1616 due to the following:

- Compliance with Regulation (EU) 10/2011 cannot always be confirmed.
- The waste not always originates from food contact applications.
- Not all plastic waste might have been subject to separate collection.
- The waste does not always originate from municipal waste or from food retail or other food businesses.

Today, recyclers that apply this novel technology for the production of BHET to be used in food contact applications only use PET waste originating from packaging. Therefore, this report only includes results of the monitoring of contaminant levels from input and output batches that were produced from this waste stream.

Irrespective of the type, mode of collection and origin of the input material, the output contains minimum 85% of BHET. Together with the identified BHET 'alike' co-products like MHET[2] (CAS# 71949-29-6), BHEI[3] (CAS# 3644-99-3), BHEET[4] (CAS# 65133-69-9), BHET[5] dimer (CAS# 2144-69-6), EG (CAS# 107-21-1) and diethylene glycol (DEG, CAS# 111-46-6) (Figure 3) that, as indicated by their structure

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[1] Post-consumer plastic waste as defined in the proposal for a Regulation on packaging and packaging waste, published on 30 November 2022 (European Commission, 2022): 'post-consumer plastic waste' means plastic waste that is generated from plastic products that have been placed on the market.
[2] TPA having reacted with only one molecule of EG
[3] isophthalic acid (IPA) having reacted with two molecules of EG
[4] TPA having reacted with one molecule of EG and one molecule of DEG
[5] BHET that has reacted with itself

and further confirmed through analysis, will be repolymerized together with the BHET output in the post-processing step, the purity of the obtained output could be considered as 99.9%.
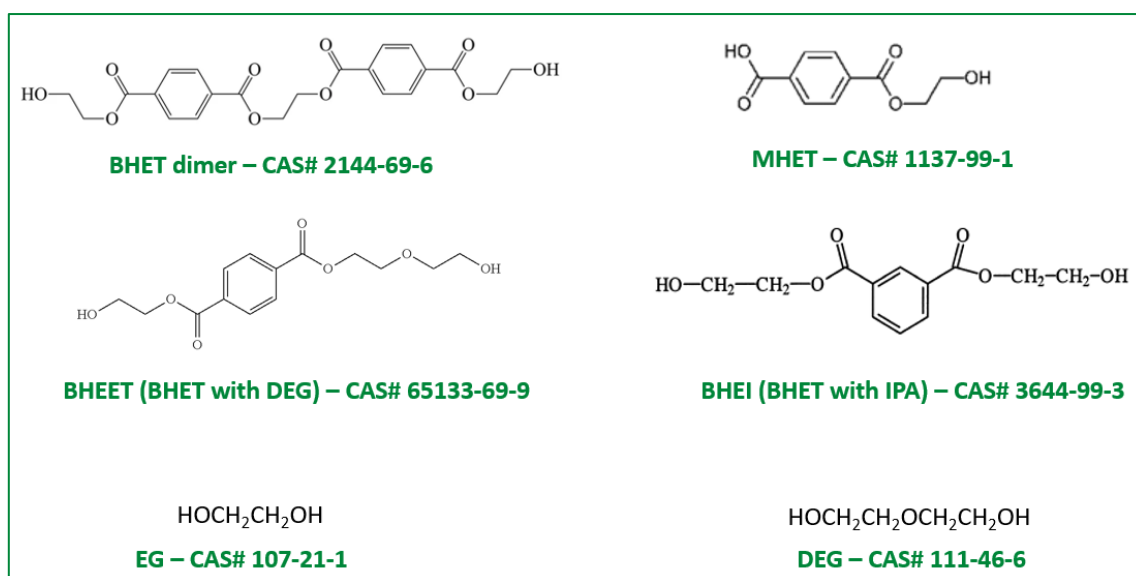

Figure 3. Main co-products formed during the glycolysis depolymerization of PET with ethylene glycol to BHET.

The specifications of the obtained BHET including its impurities are controlled inhouse at batch level using High Performance Liquid Chromatography (HPLC)[6], Gas Chromatography (GC)[7], Colorimetry[8], X-Ray Fluorescence Spectroscopy (XRF)[9] or Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[10] or Atomic Emission Spectroscopy (ICP-AES)[11], Karl Fischer Titration[12], optical microscopy and test polymerizations. Other analysis techniques may occasionally be used as well.

The output BHET is used for the manufacture of PET and its common copolyesters. Up to 100% BHET can be used for the production of PET.

The final recycled PET and its common co-polyesters are intended to be used for the manufacturing of materials and articles for contact with similar foods and under similar conditions for which virgin PET is intended:

- All types of foodstuffs;
- Hotfill and/or long term storage at room temperature and below;

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[6] HPLC: analytical technique for the separation, identification and quantification of non-volatile substances.

[7] GC: analytical technique for the separation, identification and quantification of volatile and semi-volatile substances.

[8] Colorimetry: analytical technique for the determination of the concentration of colored compounds in a solution.

[9] XRF: analytical technique for the qualitative and quantitative determination of the elemental composition of a material.

[10] ICP-MS: analytical technique for the detection and quantification of metals and several non-metals in samples at very low concentrations.

[11] ICP-AES: analytical technique for the qualitative and quantitative determination of the elemental composition of a sample.

[12] Karl Fischer titration: classic titration method to determine trace amounts of water in a sample.

- Use for microwaveable applications.

Especially in the case of its common co-polyesters, appropriate intended-use conditions should be determined and evaluated depending on the physical properties of the material.

3. Summary of the reasoning on the capability of the novel technology and the recycling processes to manufacture recycled plastic materials and articles that comply with Article 3 of Regulation (EC) No 1935/2004 and that are microbiologically safe

The pre-processing, decontamination and post-processing processes of recycling processes applying this novel technology are described in paragraph 2. The novel technology combines the transformation of the polymer into its building block BHET to facilitate the removal of all the impurities by traditional and well recognized purification techniques.

The physical processes that are used (solid/liquid separation; distillation; adsorption on active substrates; crystallization, washing and drying) are common processes used in the chemical industry to purify most of its reagents and products. They rely on robust scientific principles that are compulsory for the obtention of highly purified molecules in the medical devices and pharmaceutical industries. As a result, the BHET obtained by recycling processes that apply this novel technology is of very high purity: BHET + polymerizable co-products >99.9% as confirmed by the analysis conducted on the purified BHET output batches part of this monitoring program.

The decontamination efficiency of a recycling process using this novel technology, assessed by Welle (2021) using a challenge study, was shown to be at least > 99.94% for all surrogate contaminants. Based on this decontamination efficiency, it could be calculated that, for the non-volatile surrogate contaminants, the novel technology is able to reduce contaminant levels of minimum 1300 mg/kg in the input material down to a concentration in the output (Cmod) that would not lead to the exceedance of the dietary exposure in infants of 0.0025 µg/kg bw/day[13] (EFSA, 2011; Appendix III,C). For volatile surrogate contaminants, this calculated maximum contaminant level in the input material is lower mainly because of the limitations of the detection limit of the analytical method and the lower initial contaminant levels in the challenge test. Since the boiling points of these volatile surrogates are below the temperature of the glycolysis process and considering the different decontamination steps that are applied in this technology, it can be assumed that the decontamination efficiency for volatiles is at least as high as for non-volatiles.

Contaminant levels in post-consumer food contact PET waste is conservatively set by EFSA (2011) at 3 mg/kg PET. For non-food contact applications, Franz and Welle (2020) demonstrated that contaminants can be present in concentrations ranging from sub-mg/kg up to around 30 mg/kg on average with some exceptionally high levels of ethanol of up to 1100 mg/kg in some individual samples. These levels are lower than the contaminant levels that this novel technology can handle.

Even though the waste used by the recyclers originates from the EU market and PET production industry states that PET produced in Europe complies with Regulation (EU) 10/2011, compliance of the waste materials input with Regulation (EU) 10/2011 cannot be entirely demonstrated since a small

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[13] human exposure threshold value for chemicals with structural alerts raising concern for potential genotoxicity (Kroes *et al.*, 2004),

fraction of the plastic waste originates from non-food contact applications that do not have compulsory and specific compositional regulatory requirements. However, the obtained BHET output is 99.9% pure and is an di-ester of EG and TPA which is naturally formed during the normal production of PET. Both EG and TPA are authorized substances in Regulation (EU) No 10/2011 with identification number FCM227 and FCM785, respectively.

The BHET output produced by this novel technology can manufacture recycled plastic materials and articles that are microbiologically safe. Temperatures used during the glycolysis process and during post-processing –respectively, minimum 195°C and for minimum 1 hour and above 245°C for several hours– are more stringent than the typical conditions for sterilization used in the medical, pharmaceutical and food and beverage industry as reported by Jildeh *et al*. (2021).

4. List of all substances with a molecular weight below 1000 Dalton found in plastic input and corresponding output

As developer of the Novel Technology, PETCORE has coordinated with the recyclers the selection of the sampling strategy, the analysis to be performed and the third party laboratory. To ensure maximum comparability of the analysis results, it was decided to run the analysis at one single laboratory and therefore to collect all samples of the different Consortium members produced until the end of August 2023. For these production runs only PET waste originating from packaging was used. In total, 6 batches of plastic input material and the corresponding decontaminated BHET output samples have been analysed.

The choice of the third party laboratory was based on its experience and expertise in analysing PET samples, the state of the art of its analytical equipment and validated methods as well as the capability to identify and to risk assess non-intentionally added substances (NIAS) taking into account the specificity of this particular technology. The limit of detection (LOD) of the analysis of volatile substances was 0.01 mg/kg. However, even though the laboratory initially confirmed the limit of detection (LOD) for the analysis of semi-volatile and non-volatile substances in PET input and BHET output samples would be 0.1 mg/kg, the lab further informed that this LOD could not be reached. Therefore, the LODs for these analyses were increased to 0.85 and 8.5 mg/kg for PET input and BHET output, respectively.

The results of the analysis of substances in the plastic input and the corresponding BHET output samples can be found in Table 1. The substances detected in the samples were ordered by their relative occurrence in the input samples.

The results of the analysis of inorganic compounds and primary aromatic amines are summarized in Table 2 and 3, respectively.

Table 1. List of all organic substances with a molecular weight below 1000 Dalton in input and output samples.

Substance	MW	CAS	PET INPUT			BHET OUTPUT		
			LOQ	frequency	conc (mg/kg)	LOQ	frequency	conc (mg/kg)
acetaldehyde	44	75-07-0	<0.05	100%	0.26-0.8	<0.05	67%	0.19-0.65
ethanol	46	64-17-5	<0.01	100%	0.34-0.51	<0.01	83%	0.28-18
C20H18O9 – *possibly L[TPA+EG]2*	402		<0.85	100%	0.89-2.7	<8.5	83%	12.0-550
C[TPA/EG/TPA/DEG], C22H20O9	428	29278-57-7	<0.85	100%	2.5-10	<8.5	83%	18 -160
C[2TPA+2DEG], C24H24O10	472		<0.85	100%	4-9.8	<8.5	83%	34-260
C[TPA/EG/TPA/EG/TPA/EG], C30H24O12	576	7441-32-9	<0.85	100%	2.5-3.3	<8.5	0%	<8.5
C[TPA/EG/TPA/EG/TPA/EG/TPA/EG], C40H32O16	769	16104-96-4	<0.85	100%	2.3-3.8	<8.5	0%	<8.5
Unknown - *possibly C[TPA+EG]3+[TPA+DEG] or C[TPA+EG]3+[IPA+DEG]*	812		<0.85	100%	1.5-2.6	<8.5	0%	<8.5
several hydrocarbons			<0.01	100%	0.22-2.2	<0.01	100%	0.083-0.1
acetone	58	67-64-1	<0.01	83%	0.11-0.16	<0.01	83%	0.03-0.32
octanal	128	124-13-0	<0.01	83%	0.025-0.21	<0.01	0%	<0.01
L[TPA/EG/TPA/EG+EG], C22H22O10, PET dimer	446	2144-69-6	<0.85	83%	1.0-1.9	<8.5	100%	130-1500
Solvent Blue 104 - C32H30N2O2	474	116-75-6	<0.85	83%	2.5-77	<8.5	0%	<8.5
1-butanol	74	71-36-3	<0.01	67%	0.01-0.03	<0.01	33%	<0.01
polyproylene glycol n=7	424	25322-69-4	<0.85	67%	0.87-2.6	<8.5	0%	<8.5
2-(2H-Benzotriazol-2-yl)-4, 6-bis(1-methyl-1-phenylethyl)phenol – Tinuvin 234	448	70321-86-7	<0.85	67%	0.93-6.1	<8.5	0%	<8.5
Unknown - *possibly L[TPA+EG]3*	594		<0.85	67%	1.1-1.6	<8.5	0%	<8.5
alcohols, C12-14, ethoxylated C12		68439-50-9	<0.85	67%	2.0-16	<8.5	0%	<8.5
ethyl acetate	88	141-78-6	<0.01	50%	0.01-0.038	<0.01	17%	0.03
toluene	92	108-88-3	<0.01	50%	0.011-0.03	<0.01	0%	<0.01
xylene	106	1330-20-7	<0.01	50%	0.01-0.015	<0.01	0%	<0.01
Unknown	336		<0.85	50%	1.1-5	<8.5	0%	<8.5
polyproylene glycol n=6	366	25322-69-4	<0.85	50%	0.98-1.1	<8.5	0%	<8.5
C27H48O8	501		<0.85	50%	4.0-33	<8.5	0%	<8.5
alcohols, C9-11-iso-, C10-rich, ethoxylated		78330-20-8	<0.85	50%	7.5-31	<8.5	0%	<8.5
butanone	72	78-93-3	<0.01	33%	0.029-0.037	<0.01	0%	<0.01
Disperse Yellow 54 - C18H11NO3	289	12223-85-7	<0.85	33%	0.88-1.3	<8.5	0%	<8.5
Solvent Violet 13 - C21H15NO3	329	81-48-1	<0.85	33%	5.1	<8.5	0%	<8.5
acetyl tributyl citrate (ATBC)	402.5	77-90-7	<0.85	33%	2.4-2.6	<8.5	0%	<8.5
polyproylene glycol n=8	482	25322-69-4	<0.85	33%	1.4-1.6	<8.5	0%	<8.5
Unknown	499		<0.85	33%	3.5-3.9	<8.5	0%	<8.5
2-propanol	60	67-63-0	<0.01	17%	0.025	<0.01	17%	1.3
propyl acetate	102	109-60-4	<0.01	17%	0.04	<0.01	0%	<0.01
trichloromethane	119	67-66-3	<0.01	17%	0.06	<0.01	0%	<0.01
trichloroethylene	131	79-01-6	<0.01	17%	0.01	<0.01	0%	<0.01

Table 1. List of all organic substances with a molecular weight below 1000 Dalton in input and output samples (continued).

Substance	MW	CAS	PET INPUT			BHET OUTPUT (mg/kg)		
			LOQ	frequency	conc (mg/kg)	LOQ	frequency	conc (mg/kg)
limonene	136	138-86-3	<0.01	17%	0.32	<0.01	0%	<0.01
L[TPA+EG], C10H10O5 - MHET	210	1137-99-1	<0.85	17%	0.96	<8.5	100%	33-130
C18H39N – *possibly octadecylamine or hexadecyldimethylamine*	269		<0.85	17%	14	<8.5	0%	<8.5
polyproylene glycol n=5	308	25322-69-4	<0.85	17%	0.96	<8.5	0%	<8.5
tributyl citrate	360	77-94-1	<0.85	17%	1.8	<8.5	0%	<8.5
alcohols, C10, ethoxylated		Ref. 77708	<0.85	17%	56	<8.5	0%	<8.5
alcohols, C12-14, ethoxylated propoxylated		68439-51-0	<0.85	17%	51	<8.5	0%	<8.5
ethylene glycol	62	107-21-1	<0.01	0%	<0.010	<0.01	83%	1-33
tetrahydrofuran	72	109-99-9	<0.01	0%	<0.01	<0.01	33%	0.01-0.02
cyclohexane	84	110-82-7	<0.01	0%	<0.01	<0.01	17%	0.013
C7H6O2 – *likely benzoic acid*	122		<0.85	0%	<0.85	<8.5	33%	3.6-61
triethylene glycol	150	112-27-6	<0.85	0%	<0.81	<8.5	33%	2.7-680
C9H10O3 (with C2H4O fragment) – *likely 2-hydroxyethyl benzoate or TPA*	166		<0.85	0%	<0.85	<8.5	100%	24-94
C[TPA+EG], C10H8O4	192		<0.85	0%	<0.85	<8.5	67%	34-43
polyethylene glycol n=4	194	25322-68-3	<0.85	0%	<0.81	<8.5	17%	340
C[TPA+DEG], C12H12O5	236		<0.85	0%	<0.85	<8.5	83%	31-650
L[TPA+EG+DEG], C14H18O7 - BHEET	298	65133-69-9	<0.85	0%	<0.85	<8.5	100%	74-3500
Unknown	322		<0.85	0%	<0.85	<8.5	17%	29
C15H20O8	328		<0.85	0%	<0.85	<8.5	17%	23
L[TPA+2DEG], C16H22O8	342		<0.85	0%	<0.85	<8.5	83%	120-2700
C18H26O9	386		<0.85	0%	<0.85	<8.5	33%	6.1-100
Unknown	400		<0.85	0%	<0.85	<8.5	50%	12-32
Unknown	442		<0.85	0%	<0.85	<8.5	50%	3-43
L[2TPA+2DEG] or L[2TPA+DEG+2EG], C24H26O11	490		<0.85	0%	<0.85	<8.5	100%	80-4500
C24H26O12	506		<0.85	0%	<0.85	<8.5	17%	13
C25H28O12	520		<0.85	0%	<0.85	<8.5	17%	25
L[2TPA+EG+2DEG], C26H30O12	534		<0.85	0%	<0.85	<8.5	67%	23-1300
L[3TPA+2EG+DEG] or L[3TPA+4EG] C32H30O14	639		<0.85	0%	<0.85	<8.5	67%	2.3-110
L[3TPA+DEG+3EG], C34H34O15	683		<0.85	0%	<0.85	<8.5	50%	2.7-130
Unknown, with EG moieties	826		<0.85	0%	<0.85	<8.5	17%	19

Table 2. Summary of the results of the analysis of inorganic compounds*

Element	PET INPUT (Reflux/Microwave)			BHET OUTPUT (Reflux/Microwave)		
	LOD	frequency	conc (mg/kg)	LOD	frequency	conc (mg/kg)
Al	0.061-0.095/1.4-1.9	17%/83%	490/<5-11	0.067-0.091/1.5-1.9	0%/17%	ND/8.6
Sb**	0.061-0.095/1.4-1.9	100%/100%	0.97-1.9/210-310	0.067-0.091/1.5-1.9	100%/50%	<0.25-4.1/<4.5-<5.4
As	0.061-0.095/1.4-1.9	0%/0%	ND/ND	0.067-0.091/1.5-1.9	0%/0%	ND/ND
Ba	0.061-0.095/1.4-1.9	100%/0%	<0.29/ND	0.067-0.091/1.5-1.9	100%/0%	<0.20-<0.27/ND
Pb	0.061-0.095/1.4-1.9	0%/0%	ND/ND	0.067-0.091/1.5-1.9	0%/0%	ND/ND
Cd	0.0061-0.0095/0.14-0.19	0%/0%	ND/ND	0.0067-0.0091/0.15-0.19	17%/0%	<0.027/ND
Ca	6.1-9.5/140-190	100%/0%	27-110/ND	6.7-9.1/150-190	83%/0%	<25-110/ND
Cr	0.061-0.095/1.4-1.9	33%/17%	<0.18-<0.23/<5.6	0.067-0.091/1.5-1.9	33%/0%	<0.23/ND
Co	0.061-0.095/1.4-1.9	0%/33%	ND/<4.7-<5.6	0.067-0.091/1.5-1.9	0%/0%	ND/ND
Fe	0.061-0.095/1.4-1.9	100%/100%	1.5-34/<4.7-33	0.067-0.091/1.5-1.9	100%/67%	<0.25-4.9/<4.8-6.1
Eu	0.01-0.016/0.24-0.31	0%/0%	ND/ND	0.011-0.015/0.25-0.31	0%/0%	ND/ND
Gd	0.01-0.016/0.24-0.31	0%/0%	ND/ND	0.011-0.015/0.25-0.31	0%/0%	ND/ND
K	6.1-9.5/140-190	100%/100%	<18-<29/<430-<560	6.7-9.1/150-190	100%/100%	<20-<27/<450-<560
Cu	0.061-0.095/1.4-1.9	100%/67%	<0.18-0.3/<5.2-21	0.067-0.091/1.5-1.9	50%/0%	<0.23-<0.27/ND
La	0.01-0.016/0.24-0.31	0%/0%	ND/ND	0.011-0.015/0.25-0.31	0%/0%	ND/ND
Li	0.061-0.095/1.4-1.9	17%/0%	<0.2/ND	0.067-0.091/1.5-1.9	0%/0%	ND/ND
Mg	6.1-9.5/140-190	0%/0%	ND/ND	6.7-9.1/150-190	0%/0%	ND/ND
Mn	0.061-0.095/1.4-1.9	83%	<0.085-0.28/ND	0.067-0.091/1.5-1.9	33%/0%	<0.27-1/ND
Na	6.1-9.5/140-190	100%	<18-<29/ND	6.7-9.1/150-190	100%/0%	<25-70/ND
Ni	0.061-0.095/1.4-1.9	0%/33%	ND/<4.7-9.9	0.067-0.091/1.5-1.9	0%/0%	ND/ND
Hg	0.031-0.048/0.71-0.93	0%/0%	ND/ND	0.033-0.045/0.74-0.93	0%/0%	ND/ND
Tb	0.01-0.016/0.24-0.31	0%/0%	ND/ND	0.011-0.015/0.25-0.31	0%/0%	ND/ND
Zn	0.061-0.095/1.4-1.9	100%	<0.23-1.2/ND	0.067-0.091/1.5-1.9	100%/0%	<0.20-0.48/ND
Cr VI	0.061-0.095/1.4-1.9	0%/0%	ND/ND	0.067-0.091/1.5-1.9	0%/0%	ND/ND
Sum La /Eu/Gd/ Tb	0.041-0.064/1.0-1.4	0%/0%	ND/ND	0.044-0.06/0.99-1.2	0%/0%	ND/ND
Se	0.061-0.095/1.4-1.9	0%/0%	ND/ND	0.067-0.091/1.5-1.9	0%/0%	ND/ND
B	0.061-0.095/NA	100%/NA	1.8-7.8/NA	0.067-0.091/NA	100%/0%	2.2-6.9/NA
P	0.061-0.095/1.4-1.9	100%/67%	0.56-2.7/0.93-11	0.067-0.091/1.5-1.9	83%/0%	1.5-3.6/ND
Br	0.061-0.095/1.4-1.9	100%/83%	<0.18-<0.29/3.5-7.5	0.067-0.091/1.5-1.9	100%/83%	<0.23-0.46/8.2-15

*Summary of results obtained with 2 different methods for sample preparation: digestion with reflux and microwave (see section 9).

** Since antimony concentrations in PET beverage bottles and pre-forms from the European market were determined to be in the range of 70-290 mg/kg (Welle and Franz, 2011), it is assumed that the reflux digestion method is not appropriate for the analysis of antimony in PET.

LOD: limit of detection; ND: not detected; NA: not analysed

Table 3. Summary of the analysis of primary aromatic amines

Substance	PET INPUT			BHET OUTPUT		
	LOD (µg/kg)	frequency	conc (µg/kg)	LOD (µg/kg)	frequency	conc (µg/kg)
total primary aromatic amines	<62	17%	130	<62	50%	<120
aniline	<5	0%	<5	<5	17%	120
p-toluidine	<5	0%	<5	<5	17%	11
all other substances	<5	0%	<5	<5	67%	<5

5. List of contaminating materials regularly present in the plastic input

Table 4 lists the contaminating materials regularly present in the plastic input.

Table 4. Contaminating materials regularly present in the plastic input.

Contaminant	Value (wt% in input)
Polyolefins	<10
Other polymers (PVC, PA, EVOH, PS)	<1
Inert materials	≤5
Fillers like carbon black, talc,…	<5

The fraction of plastics not intended for contact with food in the plastic input in this report is below 5%.

The output is 99.9% BHET and co-products and does not contain other materials.

6. Analysis of the likely origin of the identified contaminants identified in paragraph 4 and 5

Input material

Depending on the collection and sorting process, post-consumer PET waste can contain a limited amount of other polymers and materials like polyolefins, polyvinyl Chloride (PVC), polyamide (PA), ethylene vinyl alcohol (EVOH), polystyrene (PS) and fillers. These polymers and materials originate from the following sources:

- Polyolefins like polyethylene (PE) and polypropylene (PP) are used to manufacture bottle closures and present in a wide range of other plastic products, including bottle labels

- PVC is used in the manufacturing of certain labels and sleeves for bottles.

- PS is used in disposable cups and other packaging materials.

- EVOH is used as oxygen barrier in flexible and non-flexible food packaging.

- PA is often used as barrier layer in flexible packaging films.

- Fillers are used in many plastic packaging materials to modify their properties and enhance their performance.

The likely origin of the substances detected in the input material (Table 1) is the following:

- Acetaldehyde: PET degradation product formed during injection molding.

- Ethanol, butanone, 1-butanol, toluene, xylene, octanal: substances reported to be present in PET bottles used for non-food products like dishwashing agents or sanitary and personal hygiene products (Franz and Welle, 2020).

- Limonene: since a large fraction of PET bottles is used to pack flavoured beverages, the flavour substance limonene is found in nearly all post-consumer PET waste streams (Franz et al., 2004).

- Solvent blue 104 and solvent violet 13 and disperse yellow 54: dyes used in the production of plastic articles.

- Polypropylene glycols: can be used in different applications including some pharmaceuticals and personal care products.

- Tinuvin 234: UV adsorber commonly used for the protection of polyolefin-based packaging.

- Acetyl tributyl citrate (ATBC): plasticizer used in for example cling wrap, could also be a flavouring ingredient.

- Linear and cyclic PET oligomers: substances formed during the PET polymerisation process.

Output material

The likely origin of the substances detected in the BHET output material (Table 1) is the following:

- BHET co-products: co-products of the PET depolymerization process such as BHEET, MHET, PET dimer and other BHET-like, PET dimer and trimer like substances.

- Acetaldehyde: side reaction product of EG formed during the heating of EG.

- Benzoic acid and benzoic acid ethylene glycol ester: Depolymerization products of PET degradation products.

- Ethanol, acetone, tetrahydrofuran: the origin could not be established but as these substances are typical laboratory solvents, contamination of the samples in the laboratory cannot be excluded. THF can also be formed by degradation of poly butylene terephthalate (PBT).

7. Estimation of the migration level of contaminants to food

Since the output of the recycling process is BHET, a starting substance that will undergo a further polymerization process to produce the final PET polymer, the estimation of the migration level to the food of all substances detected in the BHET is not representative of what would migrate to the food. Also during the assessment of the suitability of the purity of a starting substance in the production of a virgin plastic polymers in accordance with the requirements of article 8 of Commission Regulation (EU) No 10/2011, impurities present in the starting substances are risk assessed and this risk

assessment includes an assessment of the behavior of these impurities during the polymerization process.

As mentioned in section 2 and in the dossier with detailed information on the novel technology[14], the output of processes that apply this Novel Technology is BHET and other depolymerization co-products that, taking into consideration their chemical functional groups, will repolymerize during the PET production process (post-processing process). Therefore, they will no longer be present in the final PET polymer and the evaluation of the migration into the food is irrelevant. An assessment of the structure of the substances detected in the BHET output samples (Table 1) indicates that the majority of these substances are depolymerization co-products. These include ethylene glycol, triethylene glycol, MHET, BHEET, PET dimer and linear and cyclic PET oligomers.

However a minority of the substances detected in the BHET output samples are not depolymerization co-products. For those substances, a worst case calculation was made assuming full migration into the food (Table 5). In comparison with the migration limits set in Regulation (EU) No 10/2011, it is demonstrated that these substances, if they still would be present in the PET polymer, they are not present at levels that would endanger human health.

Table 5. Worst case migration of volatile contaminants present in the BHET output samples.

Substance	MW	CAS	BHET OUTPUT		
			conc in output (mg/kg)	worst case migration* (mg/kg food)	restriction/risk assessment
acetaldehyde	44	75-07-0	0.19-0.65	0.015-0.052	FCM128 - SML=6 mg/kg
ethanol	46	64-17-5	0.28-18	0.022-1.44	FCM113 - OML=60 mg/kg
acetone	58	67-64-1	0.03-0.32	0.002-0.026	FCM119 - OML=60 mg/kg
2-propanol	60	67-63-0	1.3	0.104	FCM118 - OML=60 mg/kg
tetrahydrofuran	72	109-99-9	0.01-0.02	0.001-0.002	FCM246 - SML=0.6 mg/kg
cyclohexane	84	110-82-7	0.013	0.001	Max migration level>60 mg/kg based on DNEL
ethyl acetate	88	141-78-6	0.03	0.002	FCM327 - OML=60 mg/kg
C7H6O2 – *likely benzoic acid*	122	65-85-0?	3.6-61	0.288-4.96	FCM116 - OML=60 mg/kg

* Considering 250 ml beverage filled in a PET bottle of 20g

A few substances detected in the BHET output samples could not yet been identified by the third-party laboratory at the time of reporting. The non-identified substances are higher molecular weight substances -between 320 g/mol and 826 g/mol- which were only sporadically detected in the samples (mostly in only 1 out of the 6 samples). Even if earlier studies indicate that all impurities present in the BHET output samples are removed during the polymerization into PET and that only some PET oligomers are formed, this report provides a risk assessment, based on the worst case approach, that these unidentified substances will not polymerise and that they are potentially genotoxic. A migration

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[14] Dossier submitted on 7 April 2023 as required under Article 10(3) of Commission Regulation (EU) 2022/1616

limit of 0.017 µg/kg food (genotoxic substances, infants scenario)[15] is taken, and migration conditions of 365 days at 25°C, similar to what EFSA applies for the evaluation of mechanical recycling processes (EFSA, 2011).

For semi-volatile substances, EFSA (EFSA, 2011) made a conservative estimate (based on generally recognized Ap-based migration modelling) of the substance concentration threshold above which the migration limit of a substance in PET would be exceeded (Cmod). For a substance of 298.5 g/mol, this threshold corresponds to a concentration of 0.32 mg/kg PET. Using the decontamination efficiency of the PET polymerisation process that is at least 99.9% (Welle, 2008), the concentration of unidentified semi-volatile substances in BHET can then be 320 mg/kg. The concentration of the 3 unidentified semi-volatile substances (MW of 322, 328 and 386) is 10 times lower than this.

For molecules with higher molecular weights (> = 400), it is expected that the PET polymerization process – typically molten state polymerization followed by solid state polymerization – will still have a certain decontamination efficiency, but published data or models are not yet available. Therefore, as a worst case scenario, the efficiency is assumed to be zero. Migration modelling conducted with the commercially available software package SML Advanced version 4.54 (AKTS AG Siders, Switzerland)[16] and using a realistic activation-energy (Ea)-based model (Welle, 2013; Ewender and Welle, 2022)[17] indicates that the Cmod of a substance with a molecular weight of 400 g/mol is 90 mg/kg. For substances with higher molecular weights, this concentration is higher (Table 6). None of the unidentified substances detected in the BHET samples with a molecular weight around 400 g/mol exceeds this concentration.

Table 6. Maximum concentration of organic compounds in a PET container (1000 ml, 600 cm^2) at 25 °C, which corresponds to a migration of 0.017 µg/l.

Molecular weight (g/mol)	Substance	Maximum concentration in PET (mg/kg)
400	Fictive	90
450	Fictive	157
500	Fictive	261
750	Fictive	1804
1000	Fictive	6989

The results of the worst case calculation of the migration of inorganic compounds detected in the output BHET samples can be found in Table 7.

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[15] This concentration is derived by EFSA from the Threshold of Toxicological Concern (TTC) concept threshold limit for genotoxic compounds of 0.0025 µg/kg bw/day for an infant with 5 kg body weight (bw), which consumes 0.75 l water per day.

[16] https://www.akts.com/sml/specific-migration-limits-diffusion-migration-multilayerpackaging-short-description/

[17] A prediction model based on experimentally determined activation energies of diffusion was established. This activation energy based model predicts diffusion coefficients more precisely. The overestimation factor of this activation-energy based prediction model compared to 263 experimentally determined diffusion coefficients for 66 individual substances is 1.3 in average. However, as a worst case approach, this factor of overestimation was not applied to calculate the Cmod.

For antimony, the result of the worst case migration calculation is higher than the specific migration limit (SML). However, Welle and Franz (2011) showed that, due to the extremely low diffusion coefficients of antimony species in PET, the SML will not be exceeded under standard use of PET at room temperature and/or hotfill conditions with antimony concentrations up to 350 mg/kg.

Cadmium was detected in one sample but the level was below the limit of quantification (LOQ). Worst case migration calculation (assuming 100% migration) using the LOQ as the concentration for the calculation gives a specific migration just above the limit (SML). However, since the actual concentration level that has been detected is below the LOQ, compliance with the SML can be assumed.

Table 7. Worst case migration of inorganic substances detected in the BHET output samples*.

Element	BHET OUTPUT			EU 10/2011 - Annex II (SML (mg/kg food))
	frequency	conc (mg/kg)	worst case migration** (mg/kg food)	
Al	17%	8.6	0.688	1
Sb	100%	<0.25-<5.4	<0.02-<0.432	0.04
Ba	100%	<0.20-<0.27	<0.0016-<0.0216	1
Cd	17%	<0.027	<0.00216	0.002
Ca	83%	<25-110	<2-8.8	60
Cr (total)	33%	<0.23	<0.0184	3.6
Cr VI	0%	<0.061-<0.095	<0.00488-<0.0076	ND (0.01)
Fe	100%	<0.25-6.1	0.02-0.488	48
K	100%	<20-<560	<1.6-<44.8	60
Cu	50%	<0.23-<0.27	<0.0184-<0.0216	5
Mn	33%	<0.27-1	<0.0216-0.08	0.6
Na	100%	<25-70	<2-5.6	60
Zn	100%	<0.20-0.48	<0.016-0.0384	5
B	100%	2.2-6.9	0.176-0.552	/
P	83%	1.5-3.6	0.12-0.288	/
Br	100%	<0.23-15	<0.0184-1.2	/

* Combination of results obtained with 2 different methods for sample preparation: digestion with reflux and microwave (see section 9)
** Considering 250 ml beverage filled in a PET bottle of 20g
SML: specific migration limit

Using the same worst case calculation, the migration of detected primary aromatic amines was below the limits specified in Annex II of plastics regulation (EU) No 10/2011.

8. Sampling strategy

For this first monitoring report, samples of all produced BHET output batches and of their corresponding input batch were collected. All samples were analytically screened for the following substances:

- Volatile substances,
- Semi-volatile substances,
- Non-volatile substances,
- Inorganic substances,
- Primary aromatic amines.

The analytical screening was performed by a third party analytical laboratory selected on the basis of its experience and expertise in analysing PET samples and state of the art of its analytical equipment and validated methods.

9. Analytical procedures and methods

Samples of plastic input batches and their corresponding output batches were labelled for traceability purposes and shipped in clear and hermetically sealed containers.

The analytical procedures and method used for the analysis of the samples as well as their limits of detection and quantification are summarised in Table 8.

Volatile substances were identified using the MS database NIST. Non-volatile substances were compared to the laboratory's internal compound database and library. The quantification of identified substances was performed via the average of the external standards UV-234 (2-(2HBenzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol, CAS 70321-86-7) and Reserpine (CAS 50-55-5) for positive ESI and Irganox 1098 (CAS 23128-74-7) for negative ESI. The laboratory did not report results of the analysis of semi-volatile substances due to problems with oversaturation of the MS detector with polyester oligomers and BHET. However, since some substances like triethylene glycol that typically would be detected with a semi-volatiles GC-MS analysis method were also detected in the LC-MS analysis run, it is assumed that the overlap between the two methods allows for the majority of substances to be detected. For future monitoring reports, alternative analysis methods will need to be selected for semi-volatile substances to demonstrate that all potential substances present in input and output are detected. In addition, the analytical detection limit for the analysis of non-volatile substances in the BHET output samples was higher than expected by the third party laboratory due to the high BHET content in the samples. Alternative methods and/or third party laboratory will be selected for the next monitoring report in an attempt to lower the limit of detection.

For the screening for primary aromatic amines a dedicated method was used as the concentration level of interest is so low that general non-target screening methods cannot detect them (Nerin *et al*., 2022).

Inorganic substances were analysed using ICP-MS which is a sensitive elemental analysis technique that detects trace metals and non-metals at ultralow concentrations. The samples were initially analysed after acid digestion in nitric acid for 1 hour at reflux temperature. However, as this sample preparation did not fully dissolve the product, the analysis was repeated after acid digestion with nitric acid in the microwave. Results of both methods have been reported.

The application/covering ranges of some of the above used methods sometimes overlap but the sensitivity of the methods is different. Where the same substance was detected by different methods, the highest concentration from both analyses was reported in paragraph 4.

Table 8. Applied analytical procedures and methods including their limits of detection and quantification.

	Sample preparation	Analytical method	LOD/LOQ	
			Input	**Output**
Non-target screening of volatile substances	/	Headspace-GC/MS, 1h@200°C	LOQ: 0.01 mg/kg	LOQ: 0.01 mg/kg
Non-target screening of semi-volatile substances	Extraction with tetrahydrofuran, 1h 60°C plus ethanol	GC/MS-QToF/FID	/	/
Non-target screening of non-volatile substances	Extraction with acetonitrile, 6h reflux	LC/MS-QToF pos + neg mode	LOQ: 0.85 mg/kg	LOQ: 8.5 mg/kg
Total primary aromatic amines	Extraction in 3% acetic acid, 1h@100°C	VIS, photometry	LOD: 62 µg/kg	LOD: 62 µg/kg
Targeted analysis of primary aromatic amines	Extraction in 3% acetic acid, 1h@100°C	LC-HRMS	LOD: 5 µg/kg (REACH 22)	LOD: 5 µg/kg (REACH 22)
Targeted analysis of inorganic substances (Annex II of EU 10/2011)	Digestion with nitric acid for 1 h at reflux temperature	ICP-MS	LOD: between 0.0061 mg/kg and 9.5 mg/kg	LOD: between 0.0067 mg/kg and 9.1 mg/kg
Targeted analysis of inorganic substances (Annex II of EU 10/2011)	Microwave digestion with nitric acid	ICP-MS	LOD: between 0.14 mg/kg and 190 mg/kg	LOD: between 0.15 mg/kg and 190 mg/kg

GC: Gas chromatography; MS: Mass spectroscopy; QToF: Quadrupole- time-of-flight; FID: Flame Ionisation Detector; LC: liquid chromatography; HRMS: High Resolution MS; ICP: Inductively Coupled Plasma
LOD: limit of detection; LOQ: limit of quantification

10. Discrepancies between expected contaminant levels and the decontamination efficiency

As indicated above, the decontamination efficiency of the novel technology is at least 99.94%. With a limit of detection of the analytical methods at 0.01 mg/kg, this would mean that contaminants in the PET input material need to be present in concentrations higher than 100 mg/kg to be able to verify the decontamination efficiency. In practice, as the concentrations of contaminants in the input material are much lower, the decontamination efficiencies cannot be effectively calculated with this monitoring program.

However, no discrepancies were observed between the contaminant levels in the BHET output samples and the levels that are expected based on the dossier submitted. Only the presence of ethanol, acetone and tetrahydrofuran in the BHET output samples, even though in very low concentration and not of safety concern, is not expected and requires follow-up in the next monitoring

analysis run. As contamination in the laboratory could be at the origin, special care will be taken during sampling and shipment of the samples.

Disclaimer

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ABBREVIATIONS

BHEI	bis(2-hydroxyethyl)isophthalate
BHEET	2-hydroxyethyl[2-(2-hydroxyethoxy-)ethyl]terephthalate
BHET	bis(2-hydroxyethyl)terephthalate
Cmod	Modelled concentration
DEG	diethylene glycol
Ea	activation energy
EG	ethylene glycol
GC	gas chromatography
HPLC	high performance liquid chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
IPA	isophthalic acid
MHET	mono(2-hydroxyethyl)terephthalate
NIAS	non-intentionally added substances
PE	polyethylene
PET	polyethylene terephthalate
PP	polypropylene
PVC	polyvinyl chloride
SML	specific migration limit
TPA	terephthalic acid
XRF	X-ray fluorescence spectroscopy

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