PET Depolymerization to BHET and Purification via Crystallization

Report Monitoring Contamination Levels

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

10 April 2024 – updated 11 October 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.* On 10 October 2023, a first report discussing the monitoring data and the information as required by Article 13(5) has been published.

This report summarises the data forthcoming from the second monitoring period.

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).
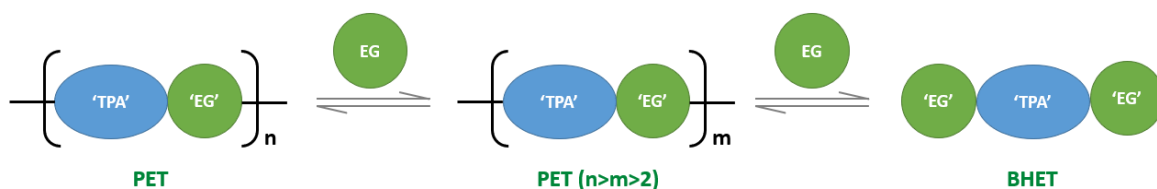
Figure 1. Schematic representation of PET glycolysis; TPA: purified terephthalic acid; EG: ethyleneglycol; BHET: bis(2-hydroxyethyl)terephthalate.

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).

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.
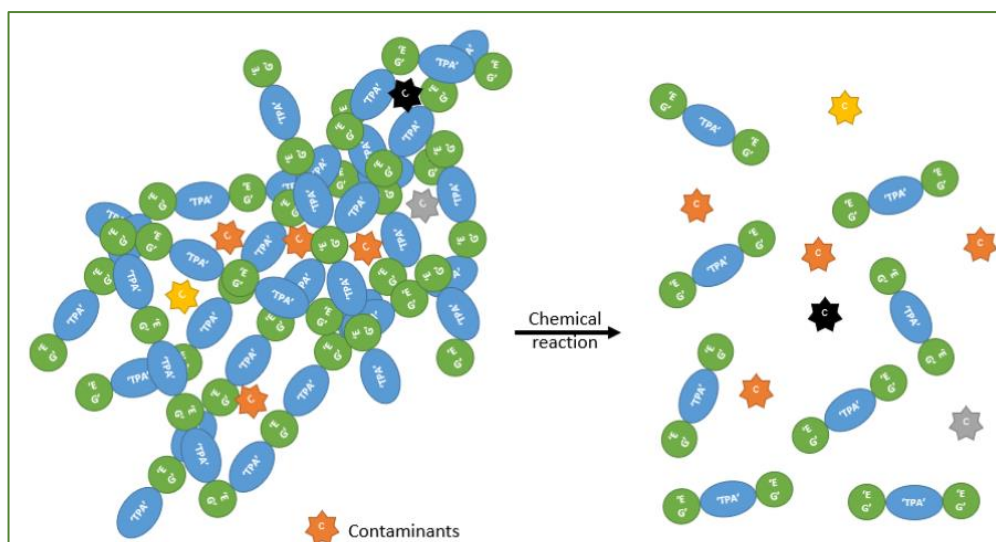- Post-consumer and post-industrial polyester textile.
- Post-consumer[1] or post-industrial PET film.

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%.
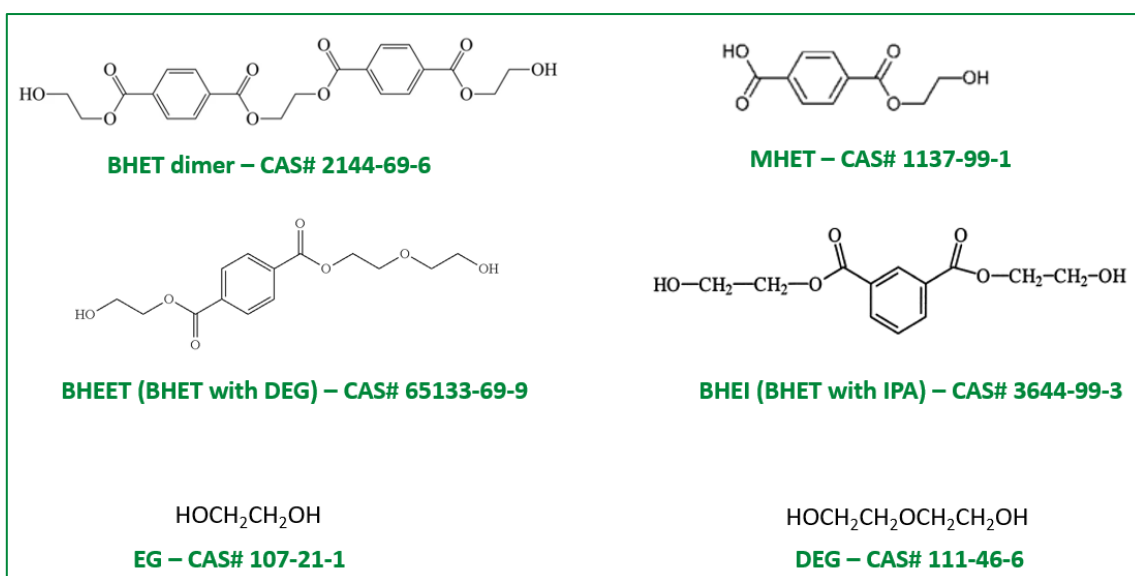

Figure 3. Main co-products formed during the glycolysis depolymerization of PET with ethylene glycol to BHET.

The specifications of the obtained BHET including its impurities are controlled 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.

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 up to 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.

Since the submission of the Novel Technology dossier, EFSA published a new scientific guidance. Following this guidance (EFSA, 2024, Appendix D, Table D.1), the maximum concentration of non-volatile substances present in the input material that can be reduced by this novel technology in the worst case scenario A is at least 1200 mg/kg (based on Cmod for methyl salicylate). For volatile surrogate contaminants, this calculated maximum contaminant level in the input material would be 67 mg/kg (based on Cmod for toluene) but the real maximum contaminant level is likely to be much higher for the same reasons as indicated above.

Contaminant levels in post-consumer food contact PET waste is conservatively set by EFSA (2024) 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

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

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 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 produce 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. In order to ensure maximum comparability of the analysis results, it was decided to perform the analysis at one single laboratory and therefore to collect all samples from the different Consortium members produced for food contact applications between the end of August 2023 and the end of March 2024. For these production runs only PET waste originating from packaging was used. In total, 3 batches of plastic input material and the corresponding decontaminated BHET output samples were 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 its capability to identify and to risk assess non-intentionally added substances (NIAS) taking into account the specificity of this particular technology. A different laboratory has been selected compared to the first monitoring period because the laboratory used for the first monitoring period experienced difficulties in achieving very low limits of detection (LOD) for semi-volatile and non-volatile substances in the PET input and BHET.

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 are summarized in Table 2.

The third party laboratory experienced issues with the analysis of primary aromatic amines in BHET. While results for primary aromatic amines were reported for all the PET input samples, results for primary aromatic amines were only reported for one of the BHET output samples. Of all the primary aromatic amines listed in entry 43 to Appendix 8 of Annex XVII to Regulation (EC) No 1907/2006, aniline is detected in one of the PET input samples. None of the aromatic amines listed in entry 43 to Appendix 8 of Annex XVII to Regulation (EC) No 1907/2006 have been detected in the corresponding BHET output sample (Table 3).

Table 1. List of all organic substances with a molecular weight below 1000 Dalton in input and output samples, sorted in descending order by their relative occurrence in the input.

Substance	MW	CAS	PET INPUT		BHET OUTPUT		Decontamination efficiency
			frequency	conc (mg/kg)	frequency	conc (mg/kg)	
Cyclic (TPA-EG)2	384.3	24388-68-9	100%	52.3±4.5 - 837±43	66%	1157±43 - 1215±24	PET-oligomer/BHET co-product
Cyclic TPA2-EG-DEG	428.4	29278-57-7	100%	396.4±19.7 - 1908±65	66%	718±65 - 1082±55	PET-oligomer/BHET co-product
n-Hexadecanoic acid (palmitic acid)	256.4	57-10-3	100%	<0.01839 – 0.42464 ± 0.58306	100%	<0.01839 – 0.07417 ± 0.00324	0 - >95.67
1,3-Dioxolane, 2-methyl-	88.11	497-26-7	67%	0.03604 ± 0.00521 – 0.902 ± 0.03438	33%	<0.03109	>73.86 - >96.55
Anethole	148.2	104-46-1	67%	<0.01176 – 0.25149 ± 0.03846	0%	<0.00356 - <0.00578	>97.7
Nonanoic acid	158.24	112-05-0	67%	0.01864 ± 0.00976 – 0.21361 ± 0.0381	33%	<0.00557 – 0.02868 ± 0.00589	>70.12 - 86.57
n-Decanoic acid	172.26	334-48-5	67%	<0.01839 – 0.08158 ± 0.01208	67%	<0.01839	>77.46
Tetradecanoic acid	228.37	544-63-8	67%	<0.01839 – 0.03027 ± 0.0345	33%	<0.01839	>81.60
Isopropyl myristate	270.5	110-27-0	67%	0.0124 ± 0.00653 – 0.0416 ± 0.01539	33%	0.046 ± 0.00381	0 - >55.08
Octadecanoic acid, butyl ester	340.6	123-95-5	67%	0.06869 ± 0.02237 – 0.08053 ± 0.00992	67%	0.06483 ± 0.00302 – 0.06599 ± 0.01322	5.62-18.05
Linear (TPA-EG)2	402.4	23186-89-2	66%	62.9±5.9 - 305±21	33%	1539±21	PET-oligomer/BHET co-product
Cyclic (TPA-DEG)2	472.4	16104-98-6	66%	<16.4 - 377±32	66%	57±12 - 177±32	PET-oligomer/BHET co-product
Linear (TPA-EG)3	594.5	16958-96-6	66%	113.5±9.0 - 984±48	33%	54±18	PET-oligomer/BHET co-product
Linear TPA3-EG2-DEG	638.6		66%	37±11 - 39±8	66%	18±11 - 57±11	PET-oligomer/BHET co-product
Cyclic (TPA3-EG2-DEG)	620.6		66%	95.8±3.6 - 1004±51	66%	30±11 - 54±11	PET-oligomer/BHET co-product
Linear (TPA-EG) (MHET)	210	1137-99-1	33%	19.2±1.6	100%	1210.6±28.5 - 35119±114 (overloaded)	PET-oligomer/BHET co-product
Cyclic (TPA-EG)	192	7337-79-3	33%	41.0±3.1	0%	<5.4	PET-oligomer/BHET co-product
Cyclic (TPA-EG)3	576.5	7441-32-9	33%	78.7±2.1	0%	<5.4	PET-oligomer/BHET co-product
2-Butenal	70.09	4170-30-3	33%	<0.1365	0%	<0.04136	
1.4-Dioxane	88.11	123-91-1	33%	<0.03109	33%	<0.03109	
Styrene	104.15	100-42-5	33%	0.19294 ± 0.02759	0%	<0.00275	>98.57
1,3-Cyclopentadiene, 5-(1-methylethylidene)-	106.16	2175-91-9	33%	0.04503 ± 0.01134	0%	<0.00275	>93.89

Cyclopentene, 1-ethenyl-3-methylene-	106.16	61142-07-2	33%	0.21861 ± 0.04876	0%	<0.00275	>98.74
Ethylbenzene	106.16	100-41-4	33%	0.08133 ± 0.02153	0%	<0.00275	>96.62
Hexanoic acid	116.16	142-62-1	33%	0.12779 ± 0.02540	33%	<0.01839	>85.61
1,3-Dioxolane, 2-propyl-	116.16	3390-13-4	33%	0.28940 ± 0.0152	33%	0.03936 ± 0.01909	>86.40
Indole	117.15	120-72-9	33%	0.05416 ± 0.01162	0%	<0.00275	>94.92
Ethanol, 2-butoxy-	118.17	111-76-2	33%	0.21138 ± 0.00942	33%	<0.03109	>85.29
Heptanoic acid	130.18	111-14-8	33%	0.02937 ± 0.00710	33%	<0.01839	>37.38
1-Hexanol, 2-ethyl-	130.23	104-76-7	33%	0.05814 ± 0.01695	0%	<0.02768	>52.39
1-Octanol	130.29	111-87-5	33%	0.32025 ± 0.00456	0%	<0.03030	>90.54
Ethanol, 2-(2-ethoxyethoxy)-	134.17	111-90-0	33%	0.21892 ± 0.07922	33%	0.09818 ± 0.07703	55.15
p-Cymene	134.22	99-87-6	33%	0.70557 ± 0.06684	0%	<0.00578	>99.18
D-limonene	136.23	5989-27-5	33%	0.7014 ± 0.06184	0%	<0.00421	>99.4
gamma-Terpinene	136.23	99-85-4	33%	0.22537 ± 0.01535	0%	<0.00578	>97.43
2-Nonanone	142.24	821-55-6	33%	0.02947 ± 0.00009	33%	<0.01839	>37.6
Nonanal	142.24	124-19-6	33%	0.07379 ± 0.1151	33%	<0.02309	>68.71
Octanoic acid	144.21	124-07-2	33%	0.12241 ± 0.02039	33%	<0.01839	>84.98
Hexanoic acid, 2-ethyl-	144.21	149-57-5	33%	<0.01839	33%	<0.01839	
Benzene, 1,2-dichloro-	147	95-50-1	33%	<0.00908	0%	<0.00275	
Estragole	148.2	140-67-0	33%	0.19526 ± 0.00161	0%	<0.00578	>97.03
2-Decanone	156.26	693-54-9	33%	0.05301 ± 0.00544	33%	<0.01839	>65.31
1-Heptanol, 2-propyl-	158.28	10042-59-8	33%	1.20137 ± 0.03846	0%	<0.03030	>97.48
Pentanedioic acid, dimethyl ester	160.17	1119-40-0	33%	<0.01839	0%	<0.00557	
Ethanol, 1-(2-butoxyethoxy)-	162.23	54446-78-5	33%	0.12269 ± 0.07845	33%	<0.01839	>85.01
2-Hydroxyethyl benzoate	166.17	94-33-7	33%	0.31653 ± 0.05501	33%	0.00965 ± 0.00261	96.95
Undecanal	170.29	112-44-7	33%	1.17517 ± 0.35322	33%	<0.007	>99.4
3-tert-Butylbenzoic acid	178.23	7498-54-6	33%	<0.01839	33%	0.03594 ± 0.00965	-
Dodecanal	184.32	112-54-9	33%	0.69111 ± 0.38746	0%	<0.007	>98.99
Dodecanoic acid	200.32	143-07-7	33%	0.13343 ± 0.02592	33%	0.0126 ± 0.00066	90.56
2,4-Di-tert-butylphenol	206.32	96-76-4	33%	0.19368 ± 0.00514	0%	<0.03030	>84.35
Ethylparaben, acetate	208.21	13031-45-3	33%	<0.1	0%	<0.03030	
Pentadecane	212.41	629-62-9	33%	<0.0137	0%	<0.00415	
Nonanoic acid, 2-pentyl ester	228.37		33%	<0.01839	33%	<0.01839	
Dodecanoic acid, ethyl ester	228.37	106-33-2	33%	0.03272 ± 0.00882	33%	<0.01839	>43.82
Phthalic acid, diisobutyl ester	278.34	84-69-5	33%	0.04047 ± 0.02519	0%	<0.00557	>86.24
Isopropyl palmitate	298.5	142-91-6	33%	0.01572 ± 0.01284	0%	<0.00557	>64.57
Phthalic acid, ethyl 2-methylbutyl ester	364.32		33%	0.09295 ± 0.02630	0%	<0.00148	>98.41

Tributyl acetylcitrate	402.5	77-90-7	33%	0.018095 ± 0.26060	0%	<0.00557	>96.92
Naphthalene	128.169	91-20-3	33%	0.01826 ± 0.00112	0%	<0.00275	>84.94
Terephthalic acid	166.13	100-21-0	0%	<5.4	33%	57.2±2.2	BHET co-product
Benzothiazole	135.19	95-16-9	0%	<0.00275	33%	0.02897 ±0.00379	-
Triethylene glycol	150.17	112-27-6	0%	<0.02768	33%	<0.09134	BHET co-product
1-Decanol	158.28	112-30-1	0%	<0.02768	33%	<0.09134	-
Ethanone, 1,1'-(1,4-phenylene)bis-	162.19	1009-61-6	0%	<0.00275	33%	0.01568 ± 0.00589	-
2-Propenoic acid, 3-phenyl-, pentyl ester	218.29	3487-99-8	0%	<0.00557	33%	<0.01839	-
Heptadecane, 2,3-dimethyl-	268.5	61868-03-9	0%	<0.00415	33%	<0.0137	-
Phthalic acid, cycloheptyl isohexyl ester	346.5		0%	<0.00557	33%	<0.01839	-

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

Element	LOD (mg/kg)	LOQ (mg/kg)	PET INPUT		BHET OUTPUT	
			Frequency*	conc (mg/kg)	Frequency*	conc (mg/kg)
Al	0.000604	0.002014	0%	ND	33%	<0.002014
Sb	0.000031	0.000105	66%	157-204±0.05	33%	1.18±0.05
Pb	0.000009	0.00003	0%	ND	0%	ND
Cd	0.000002	0.000006	0%	ND	0%	ND
Cr	0.000009	0.00003	33%	0.3	0%	ND
Co	0.000006	0.000019	33%	0.7	0%	ND
Fe	0.000886	0.002954	33%	10.9	0%	ND
Cu	0.000029	0.000098	0%	ND	0%	ND
Mg	0.000151	0.000503	0%	ND	33%	<0.000503
Mn	0.000031	0.000103	0%	ND	33%	0.32±0.05
Ni	0.000263	0.000846	66%	<0.000846	33%	<0.000846
Zn	0.000207	0.000691	33%	<0.000691	33%	<0.000691
Se	0.000300	0.001001	0%	ND	0%	ND
Ti	0.000022	0.000075	33%	5.03±0.41	0%	ND
V	0.000008	0.000028	0%	ND	0%	ND
Ge	0.000016	0.000055	0%	ND	0%	ND
Mo	0.000635	0.002117	0%	ND	0%	ND
Sr	0.000005	0.000017	33%	0.2	0%	ND
Ag	0.000006	0.000019	0%	ND	0%	ND
Tl	0.000007	0.000022	0%	ND	0%	ND

LOD: limit of detection; LOQ: limit of quantification; ND: not detected;

* results of only 2 of the 3 BHET samples due to technical issues with the analytical equipment of the third party laboratory

Table 3. Summary of the analysis of primary aromatic amines

Substance	PET INPUT			BHET OUTPUT		
	LOD (µg/kg)	frequency	µg/kg PET	LOD (µg/kg)	frequency	µg/kg BHET
aniline	0.72	33%	112.83±6.31	0.72	0%	<0.72

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 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:

- 2-methyl-1,3-dioxolane: reaction product of acetaldehyde (PET degradation product) and ethylene glycol (Kesaboina and Lofgren, 2012).

- D-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).

- γ-terpinene: major component of essential oils made from citrus fruits with strong antioxidant activity. Widely used in food, flavours and cosmetics (European Commission, 2012).

- p-cymene: abundant in several essential oils and used as a flavouring compound (European Commission, 2012).

- anethole: widely used as a flavouring substance (European Commission, 2012).

- styrene: monomer used in the manufacture of thermoplastic used in packaging materials and articles (ECHA, 2024).

- 2-(2-ethoxyethoxy) ethanol: washing & cleaning products, plant protection products, polishes and waxes, coating products, perfumes and fragrances, cosmetics and personal care products, pharmaceuticals, air care products, hydraulic fluids, inks and toners and fuels (ECHA, 2024)

- organic acids: can be formed as a result of hydration or oxidation of certain additives or additive carriers used in the production of food contact materials (fatty acid esters, polyolefin waxes and/or mineral oils). In addition, it can be by-products of complex breakdown processes that occur in residues of food/cosmetics waste.

- linear and cyclic PET oligomers: substances formed during the PET polymerization and processing steps (Hoppe *et al.*, 2017)

Output material

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

- MHET and other BHET-like, PET dimer and trimer like substances are BHET co-products.

- Terephthalic acid, triethylene glycol: PET depolymerisation and reaction products.

- Organic acids: see above.

- 2-(2-ethoxyethoxy) ethanol: see above.

- Benzothiazole: potentially a contaminant introduced by sampling, originating from a rubber sealing ring of sampling container. Is also a fragrance and a biocide.

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 substances that will polymerize or react during the PET production process. These include terephthalic acid, triethylene glycol, 2-hydroxyethyl benzoate, MHET, PET dimer and linear and cyclic PET oligomers. Most likely also the organic acids will react to the PET chain during the repolymerization process but, in the event they would remain unreacted, a risk assessment is performed

For some of the substances detected in the BHET output samples it cannot be confirmed that they will polymerize or react during the PET production process. These substances have been subject to a risk assessment:

- Hazard:
    - Several of these substances are organic acids that will most likely react to the PET chain during the repolymerization. If not, they are listed in Annex I of regulation (EU) 10/2011 as FCM 329, FCM 259, FCM304, FCM266, FCM336, FCM330, FCM348 and FCM105 without specific migration limit. The overall migration limit of 60 mg/kg food applies.
    - The toxicity of the remaining detected substances was predicted using the Toxtree software[15]. All substances were negative for genotoxic carcinogenicity and non-genotoxic carcinogenicity and none of the substances showed an alert for *S. typhimurium* mutagenicity. Most substances were classified as Cramer Class I substances with a human exposure threshold of 30 µg/kg bw/day (EFSA, 2019). Two substances were classified as Cramer Class II substances (2-nonanone and 2-decanone) with a human exposure threshold of 9 µg/kg bw/day (EFSA, 2019). Four substances were classified as Cramer Class III substances (2-methyl-1,3-dioxolane, 1,4-dioxane, 2-propyl-1,3-dioxolane and benzothiazole) with a human exposure threshold of 1.5 µg/kg bw/day (EFSA, 2019). Applying a food consumption for infants of 260g/kg bw/day (EFSA, 2017), the migration limits for Cramer Class I, II and III substances are respectively 115 µg/kg food, 35 µg/kg food and 5.7 µg/kg food.
- Exposure: The detected substances are only present in very low concentrations. The highest concentration detected for an organic acid, a Cramer Class I, a Cramer Class II and a Cramer Class III substance was, respectively, <7.3 µg/kg BHET, 98.18 µg/kg BHET, <18.39 µg/kg BHET and 39.36 µg/kg BHET. A worst case calculation assuming full migration into food[16] indicates that such low concentrations could only lead to a maximum concentration of these substances in food of <0.58 µg/kg food, 7.85 µg/kg food, <1.47 µg/kg food and 3.14 µg/kg food for organic acids, Cramer Class I, Cramer Class II and Cramer Class III substances, respectively.
- Risk assessment: since the migration limits for all detected substances are above the maximum calculated migration, none of the substances detected in the BHET output samples, for which it is uncertain whether they would polymerise in the next manufacturing step, are expected to be a safety concern.

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[14] Dossier submitted on 7 April 2023 as required under Article 10(3) of Commission Regulation (EU) 2022/1616
[15] Toxtree version v3.1.0, May 2018.
[16] Considering a worst case S/V ratio of 250 ml beverage filled in a PET bottle of 20g.

With regard to the inorganic substances detected in the BHET output samples (Table 2), only for antimony the level would exceed the migration limit established in Regulation (EU) No 10/2011 if the worst case calculation (total migration) is applied (Table 4). 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.

Table 4. 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	33%	<0.002	<0.0002	1
Sb	33%	1.18	0.094	0.04
Mg	66%	<0.0005	<000004	60
Mn	33%	0.32	0.0256	0.6
Ni	33%	<0.00085	<0.00007	0.02
Zn	33%	<0.0006	<0.00005	5

* results of only 2 of the 3 BHET samples due to technical issues with the analytical equipment of the third party laboratory
** Considering a worst case S/V ratio of 250 ml beverage filled in a PET bottle of 20g.

Applying the same worst case surface/volume ratio to the analytical detection limits of the primary aromatic amines analysis (Table 5), the migration limit of 0.002 mg/kg food set out in Annex II of Regulation (EU) No 10/2011 is not exceeded in the BHET sample for each of the primary aromatic amines listed in entry 43 to Appendix 8 of Annex XVII to Regulation (EC) No 1907/2006.

8. Sampling strategy

For this second monitoring report, samples of all produced BHET output batches and of their corresponding input batch were collected. The 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. As indicated in the first monitoring report, in order to improve the limits of detection and the baseline resolution, a different third party laboratory with alternative analytical methods was selected from the laboratory used for the first monitoring report.

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 5.

For volatile and semi-volatile compounds, identification was done using the NIST20 database (Match > 850) and retention index values (85% tolerance), which were calculated by injecting an alkane solution (C8-40) in the same conditions as the analytes. Substances were (semi-)quantified by injecting commercially available standards with known concentrations corresponding to the substances and using the same method as for NIAS screening. Calibration curves were prepared from these standards for quantification. In the absence of a pure standard of the identified substance, the identified substance was quantified with another substance of similar chemical structure.

For non-volatile substances, the identification of a substance was based on its retention time and mass spectrum, analysing commercial standards. PET oligomers were quantified with the commercially available $C_{20}H_{16}O_8$ PET oligomer standard.

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). The primary aromatic amines were analysed after migration into 3% acetic acid for 10 days at 60°C.

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 analysed after microwave digestion in a mixture of H_2SO_4 and HNO_3 (1:1).

10. Discrepancies between expected contaminant levels and the decontamination efficiency

As indicated in paragraph 3, the decontamination efficiency of the novel technology is at least 99.94%. Such a high decontamination efficiency cannot be confirmed with the relatively low levels of contaminants detected in the input materials. Even with the very low analytical detection limits of the applied analytical method which range from 1.48 to 27.68 µg/kg, the contaminants levels in the input material would have to be between 2.5 and 46 mg/kg to be able to confirm the reported decontamination efficiency. However, even though a large proportion of the contaminants detected in the input material are undetectable in the output material, the highest decontamination efficiency that can be demonstrated with the samples in this monitoring program is a decontamination efficiency of > 99.4% for D-limonene.

No discrepancies have been found between the contaminant levels in the BHET output samples and the levels that are expected based on the dossier submitted.

Table 5. Applied analytical procedures and methods including their limits of detection and quantification.

	Sample preparation	Analytical method	LOD	LOQ
Non-target screening of volatile and semi-volatile substances	PET samples: Cryogenic milling BHET samples: /	HS-SPME-GC/MS	Between 1.48 and 27.68 µg/kg PET or BHET	Between 4.88 and 91.34 µg/kg PET or BHET
Non-target screening of semi and non-volatile substances	PET samples: Cryogenic milling, dissolution in HFIP followed by precipitation of the polymer in methanol. BHET samples: solution in HFIP or ethanol	UPLC-MS-QTOF	5.4 mg/kg PET or BHET	16.4 mg/kg PET or BHET
Primary aromatic amines	Migration in 3% acetic acid, 10d@60°C	UPLC-QQQ-MS,	Between 0.19 and 8.4 µg/kg PET or BHET	Between 0.63 and 27.72 µg/kg PET or BHET
Targeted analysis of inorganic substances (Annex II of EU 10/2011)	Microwave digestion with a mixture of H_2SO_4 and HNO_3 (1:1)	ICP-MS	Between 0.002 and 0.886 µg/kg PET or BHET	Between 0.006 and 2.954 µg/kg PET or BHET

HS: Head Space; SPME: Solid phase micro-extraction; GC: Gas chromatography; MS: Mass spectroscopy; QQQ: triple quadrupole; QToF: Quadrupole- time-of-flight; UPLC: ultra-high performance liquid chromatography; ICP: Inductively Coupled Plasma; HFIP: 1,1,1,3,3,3-hexafluoroisopropanol
LOD: limit of detection; LOQ: limit of quantification

11. Differences with previous published monitoring reports

To improve the limits of detection and the baseline resolution of the analyses performed for the first monitoring report, a different third party laboratory with alternative analytical methods was selected for the second monitoring report. This resulted in the detection of an increased number of volatile and semi-volatile substances that are present at very low concentration in the BHET samples compared to the first monitoring report.

The results seem to indicate that the BHET samples in this second monitoring report contain a different mix of BHET-coproducts than the samples of the first monitoring report. It is at this point unclear whether this is due to a normal batch-to-batch variation or whether it is due to the different methodology of sample preparation between the labs used for the first and second monitoring cycles.

Disclaimer

PETCORE Europe is providing this report and related information solely as the entity representing certain business operators (the "**Business Operators**") in accordance with Articles 10.1, §2 and 13.4-5 of the Commission Regulation (EU) 2022/1616 on recycled plastic materials and articles intended to come into contact with foods (the "**Regulation**"), in the name and on behalf of said Business Operators.

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The work and this document have been prepared following the recommendations of the Pierstone Memorandum to PETCORE Europe '**Assessment of the publication of data pursuant to Regulation 2022/1616 under competition law** '.

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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