

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

Table of Contents

PET Depolymerization to BHET and Purification via Crystallization	1
1. Introduction	3
2. Brief description of the novel technology	3
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	6
4. List of all substances with a molecular weight below 1000 Dalton found in plastic input and corresponding output	7
5. List of contaminating materials regularly present in the plastic input	7
6. Analysis of the likely origin of the identified contaminants identified in paragraph 4 and 5	8
7. Estimation of the migration level of contaminants to food.....	8
8. Sampling strategy.....	9
9. Analytical procedures and methods.....	9
10. Discrepancies between expected contaminant levels and the decontamination efficiency	10
ABBREVIATIONS	12
REFERENCES.....	13

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).

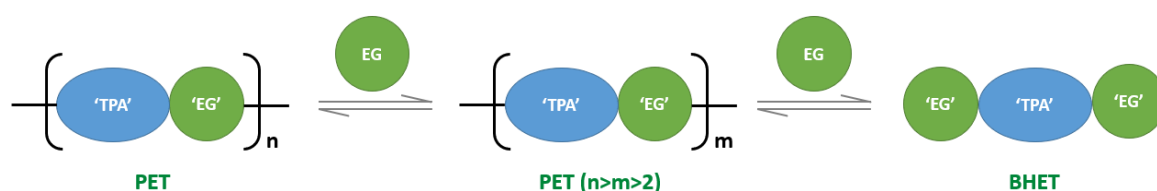


Figure 1. Schematic representation of PET glycolysis; TPA: purified terephthalic acid; EG: ethyleneglycol; BHET: bis(2-hydroxyethyl)terephthalate.

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).

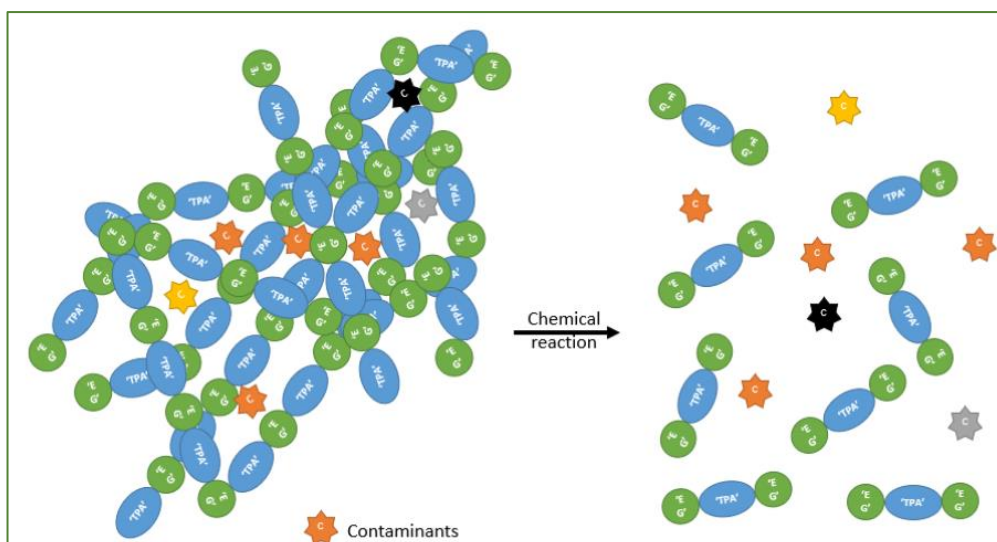


Figure 2. Schematic representation of the release of contaminants during glycolysis.

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-consumer¹ 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 MHET² (CAS# 71949-29-6), BHEI³ (CAS# 3644-99-3), BHEET⁴ (CAS# 65133-69-9), BHET⁵ 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

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%.

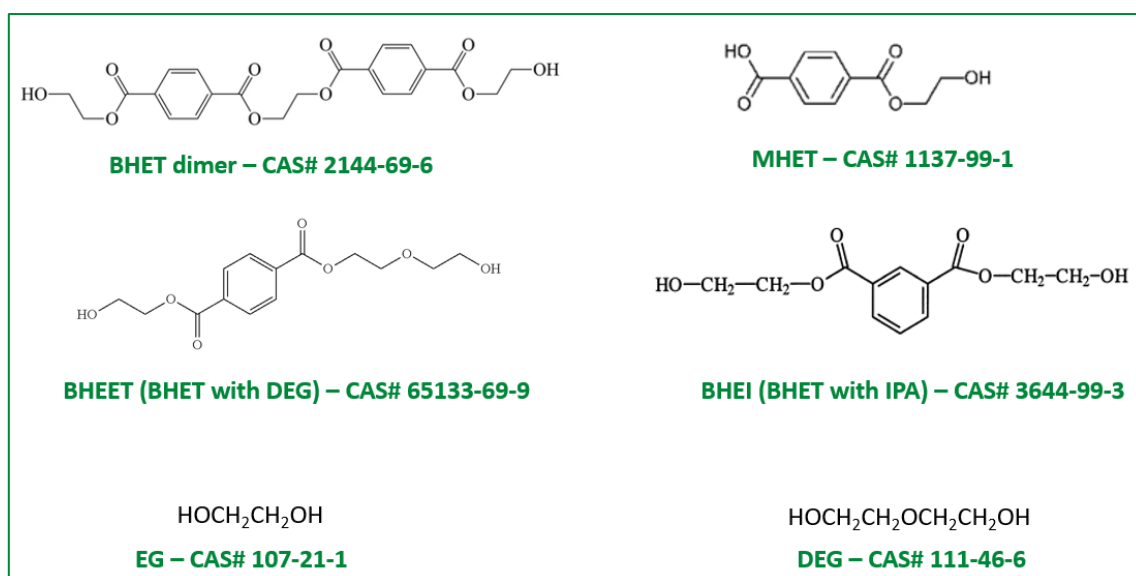


Figure 3. Main co-products formed during the glycolysis depolymerization of PET with ethylene glycol to BHET.

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, Colorimetry⁸, X-Ray Fluorescence Spectroscopy (XRF)⁹ or Inductively Coupled Plasma Mass Spectrometry (ICP-MS)¹⁰ or Atomic Emission Spectroscopy (ICP-AES)¹¹, Karl Fischer Titration¹², 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. If used at 100%, it can replace the molar equivalent of 1 TPA and 1 EG, while yielding 1 excess EG. When blended in the polymerisation reactor at lower %, BHET will replace 1TPA and 2 EG.

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:

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.

- All types of foodstuffs;
- Hotfill and/or long term storage at room temperature and below;
- 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 (C_{mod}) that would not lead to the exceedance of the dietary exposure in infants of 0.0025 µg/kg bw/day¹³ (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.

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

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 a 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. The choice of the latter one 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 particularity of this specific technology.

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 until the end of August 2023. However, due to the high number of samples received and the difficulties with analysing input material samples with high sensitive analytical equipment, the selected laboratory SQTS (Switzerland) informed the Consortium that they were unable to deliver the results within the agreed timeframe. Therefore, the report will be completed as soon as the report from SQTS is received.

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

To be completed upon reception of the SQTS analysis report.

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

Table 2 lists the contaminating materials regularly present in the plastic input.

Table 2. 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.
- 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 food packaging.
- PA is often used as barrier layer in flexible packaging films.
- Fillers are used in plastic packaging materials to modify their properties and enhance their performance.

The likely origin of the substances detected in the input material is the following:

To be completed upon reception of the SQTS analysis report.

Output material

To be completed upon reception of the SQTS analysis report.

7. Estimation of the migration level of contaminants to food

To be completed upon reception of the SQTS analysis report.

8. Sampling strategy

For this first monitoring report, samples of all produced output batches and 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 3.

Table 3. Applied analytical procedures and methods including their limits of detection and quantification.

	Sample preparation	Analytical method	LOD	LOQ
Non-target screening of volatile substances	/	Headspace-GC/MS, 1h@200°C ^a		
Non-target screening of semi-volatile substances	Extraction with dichloromethane	GC/MS-QToF/FID ^b		
Non-target screening of non-volatile substances	Extraction with acetonitrile	LC/MS-QToF pos + neg mode ^c		
Targeted analysis of primary aromatic amines	Extraction with methanol	LC-HRMS ^d		
Targeted analysis of inorganic substances (Annex II of EU 10/2011)	Pressure digestion	ICP-MS ^e		

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

Analysis of organic substances is done through a non-targeted screening of volatile, semi-volatile and non-volatile substances with different methods (Table 3).

For volatile substances, a headspace-GC-MS method is used which is a versatile technique employed in a wide range of industries and research areas to identify, quantify, and characterize volatile and

semi-volatile compounds in plastic/polymer samples. The thermal desorption conditions of 1h@200°C specifically allow the exhaustive extraction of volatile substances present in PET without degrading the sample. The detection is done by MS and the mass spectra were compared with a mass spectra library.

For semi-volatile and non-volatile substance, the samples were first extracted. The solvent and extraction conditions have been chosen to swell the polymer, without generating new substances (Nerin *et al.*, 2022). The extracts were analysed using GC/MS-QToF/FID and LC/MS-QToF for semi-volatile and non-volatile substances, respectively. High-resolution MS detectors like the QToF provide accurate masses isotopic patterns and intensities, which can lead to theoretical information about composition of fragments (Peters *et al.* 2019). This allows for the identification of unknown NIAS.

The application ranges of the above used non-targeted screening methods overlap but the sensitivity of the methods is different. In case the same substance was detected by different methods, the highest concentration of both analyses was reported in paragraph 4.

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.

All analytical methods are validated and part of the ISO17025 accreditation of the third party laboratory.

10. Discrepancies between expected contaminant levels and the decontamination efficiency

To be completed upon reception of the SQTS analysis report.

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.

PETCORE Europe has aimed to report, consolidate and accurately provide the necessary data and materials as provided in article 13.5 of the Regulation on behalf of the Business Operators (the “**Information**”). However, PETCORE Europe makes no representations or warranties regarding the completeness, accuracy or validity of such Information and does not warrant the good performance of the Business Operators’ obligations under the Regulation.

Any questions, requests, or inquiries regarding the content of this report should be directed to PETCORE Europe as the developer and representative of the Business Operators concerned.

As a mere representative, PETCORE Europe accepts no liability for any loss, damage, action, or consequence arising from the use of the Information submitted. Use and interpretation of the Information is at the sole risk and discretion of the user. Such exclusion of liability does not apply in the event of willful intent case of gross negligence of PETCORE Europe, its employees or contractors.

Unless otherwise agreed, the report and the Information it contains shall only be used under the Regulation and for the purposes provided in the Regulation.

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
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
TPA	terephthalic acid
XRF	X-ray fluorescence spectroscopy

REFERENCES

- EFSA (2011). Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF). Scientific Opinion on the criteria to be used for safety evaluation of a mechanical recycling process to produce recycled PET intended to be used for manufacture of materials and articles in contact with food. *EFSA Journal*, 9, 2184.
- Franz, R.; Mauer, A.; Welle, F. (2004). European survey on post-consumer poly(ethylene terephthalate) materials to determine contamination levels and maximum consumer exposure from food packages made from recycled. PET. *Food Addit. Contam.* 2004, 21, 265–286. <https://doi.org/10.1080/02652030310001655489>
- Franz, R.; Welle, F. (2020). Contamination levels in re-collected PET bottles from non-food applications and their impact on the safety of recycled PET for food contact. *Molecules* 2020, 25, 4998. <https://doi.org/10.3390/molecules25214998>
- Jildeh, Z.B., Wagner, P.H., Schöning, M.J. (2021). Sterilization of objects, products, and packaging surfaces and their characterization in different fluids of industry: the status in 2020. *Phys. Status Solidi A* 2021, 218, 2000732. <https://doi.org/10.1002/pssa.202000732>
- Kroes, R., Renwick, A.G., Cheeseman, M., Kleiner, J., Mangelsdorf, I., Piersma, A., Schilter, B., Schlatter, J., van Schothorst, F, Vos, J.G., Würtzen, G. (2004). Structure-based thresholds of toxicological concern (TTC): guidance for application to substances present at low levels in the diet. *Fd. Cosmet. Toxicol.*, 42: 65-83.
- Nerin, C., Bourdoux, S., Faust, B., Gude, T., Lesueur, C., Simat, T., Stoermer, A., Van Hoek, E., Oldring, P. (2022). Guidance in selecting analytical techniques for the identification and quantification of non-intentionally added substances (NIAS) in food contact materials (FCMS). *Food Additives & Contaminants: Part A*, vol 39(3): 620-643. <https://doi.org/10.1080/19440049.2021.2012599>
- Peters, R.J.B., Groeneveld, I., Sanchez, P.L., Gebbink, WŞ., Gersen, A., de Nijs, M., van Leeuwen, S.P.J. (2019). Review of analytical approaches for the identification of non-intentionally added substances in paper and board food contact materials. *Trends Food Sci Technol.* 85:44–54. <https://doi:10.1016/j.tifs.2018.12.010>.
- Welle, F. (2021). Safety Evaluation of Polyethylene Terephthalate Chemical Recycling Processes. *Sustainability* 2021, 13, 12854. <https://doi.org/10.3390/su132212854>