

Deliverable D4.8

Report on up-scaled validation of recovered materials in other industries



Feasible Recovery of critical raw materials through a new circular Ecosystem for a Li-Ion Battery cross-value chain in Europe

WP 4 - Scaling and validation of feasible technologies

D4.8 - Report on up-scaled validation of recovered materials in other industries

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Versions

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List of Abbreviations

ACRONYMS	DESCRIPTION
ABS	Polyacrylonitrile-Butadiene-Styrene
EoL	End of Life
EV	Electric Vehicle
FTIR	Fourier Transform Infrared spectroscopy
HDPE	High Density Polyethylene
NIR	Near-infrared
PA	Polyamide
PC	Polycarbonate
PPE	Polyphenylene ether
PP	Polypropylene

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1. Executive summary

This deliverable presents results of revalorization of valuable precursors and black mass within alternative material. FREE4LiB address use in other fields to minimize risks in case black mass were not useful for active materials. The use of black mass and precursor recovery in other sectors is of high interest reducing the dependency on metal oxides from outside EU. Specifically, D4.8 addresses the upscaled synthesis of ceramic pigments starting from recycled materials and the recycling of plastics. Deliverable shows viability of the recycling in specific fields

2. Introduction

FREE4LiB aims to develop at TRL 5-6 technologies to achieve 6 new sustainable and efficient processes to recycle end-of-life (EOL) LIBs (dismantling, pre-treatment and 4 materials recovery processes) delivering very innovative recycling solutions to reach highly efficient materials recovery (metal oxides, metals and polymers) improving the supply of secondary resources at EU level. FREE4LiB also will deliver technologies to improve 3 processes aiming at metals and polymers re-using and electrode synthesis on the same value chain as secondary raw materials for re-manufacturing greener batteries, and it will study options to harness non-reusable elements in other fields FREE4LiB will also deliver a methodology based on the Battery Passport principles to improve processes traceability.

Within scope of the project, the WP4 focuses on development of material technology for recovery of valuable materials and their valorisation within the battery value chain. In WP4 task 4.11 starts from task 3.9 and 3.10 focusing on alternative applications.

Task 4.11 studies the viability of recycled cobalt, nickel, manganese precursors in alternative industries on larger scale and recovery of thermoset materials Ceramic sector is an important industry at European level, including ceramic tiles, tableware, sanitaryware pigment production and frit production, with over 800 M m²/ year only Tiles Within Ceramic sector metal oxides are used on different applications like ceramic pigments for tile, glass, table ware decoration, for frits used in enamelling steel for household appliances, protective coatings. The use of revalorized sources for metal oxides like NiO, MnO₂ and CoO will reduce dependency from outside EU as well as reduce GHG emissions allocated to transport. In addition, as social aspect, the reduction of CoO from mining will impact also on the current situation of CoO mining related to childhood use in industrial mining. Plastic industry is another key sector. According



Plastic Europe it accounts for 398 Bn €, having 15 % of recycled plastic in circulation.

3. Objectives.

The specific objectives of the deliverable 4.8 are to present results on:

- 1- Evaluation of the black mass and recycled materials as alternative source for metal oxides in ceramic materials, specifically ceramic pigments and frits. Precursors recycled have been used in ceramic pigments, upscaling the process to 1 kg and 300-500 gr frits.
- 2- Apply thermal valorisation techniques for the recycling and recovery of thermoset plastic fractions.

4. Advances in materials use in other fields.

4.1 Recovery of metal oxides for ceramic pigments.

Ceramic pigments are inorganic structures based on spinels (CoAl_2O_4), ferrites (FeNiMnCrO , NiFeO_3), cassiterite (SnCaSbO_2), or vanadates (BiVO_4) that use metal oxides such as CoO , Fe_2O_3 , MnO_2 , NiO and CuO . Ceramic pigments are widely used in ceramics, the glass and in plastic industries.

Black pigment (NiCrCoFeMnO) was selected as structure to upscale the use of precursors. In WP4 diverse types of precursors were supplied to Torrecid, CP021 from CARTIF, precursor mixture from FIWKS and precursors from CSIC. Due to higher graphite content in material from FIWKS, CP021 and CSIC S3-BM06 were used for pigment upscaling, advancing from results achieved in WP3.

Table 1 shows chemical analysis of CP021 received compared to first sample tested in WP3. CP021 is obtained through direct delamination by CARTIF.



Table 1 CP021 composition

OXIDE	CP021-1	CP021-2
Li ₂ O	11,1	9,2
MnO ₂	14,2	16,3
CoO	10,5	13,3
NiO	63,9	59,8
Al ₂ O ₃	0,3	1,3

Two pigments were produced with CP021-2 substituting the NiO at 100 % and 50%, being the NiO content about 7% in pigment.

Synthesis process is based on mixing of raw materials, dry milling, pressing of the mixture and sintering at 1300 °C. Afterwards the pigment was jet milled, by dry milling to 5 microns.

The figure 1 below shows the X ray diffraction of obtained pigments

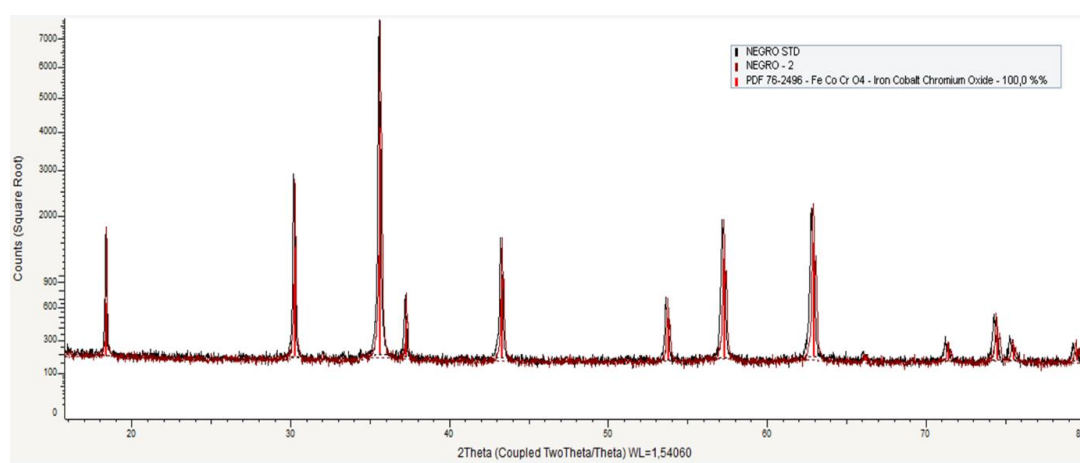


Figure 1. XRD pattern for pigments

The pigment was used in a ceramic glaze at 4 %, applied to biscuit and fired. On final glaze layer the colorimetric properties were measured. Data shows viability in use, as shown in table 2 where colorimetric properties are shown.

Table 2 Colour development

	L	A	b
Std	26,58	0,9	0,3
100% Substitution	26,67	0,78	0,19
50% Substitution	26,71	0,76	0,11

Currently pigments are used in ceramic inks for digital application. A ceramic black ink was prepared using the 100% substituted pigment. The process is based on composition mixing, milling to final particle size below 300 nm. Viscosity of ink was adjusted by optimization of dispersing agents Table 3 below shows the used composition.

Table 3 Ink composition

	%
Ceramic pigment	30-40
Solvent (glycol mixture)	40-60
Dispersing additives	3-5
Wetting agent	1-2
Defoamer	0,1-0,5

Figure 2 shows the particle size of final ink.

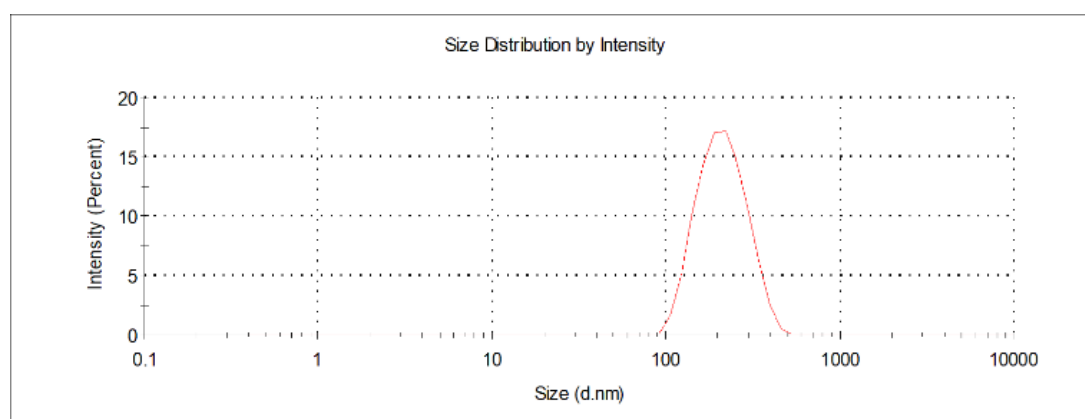


Figure 2. Ink particle size

The ink once prepared was filtered. The ink was printed and compared with standard black ink as displayed below. Using the novel ink and CMY inks a printing test was carried out printing a colour chart used for image preparation, The colour chart was used and an imagen 4 shown below was printed,

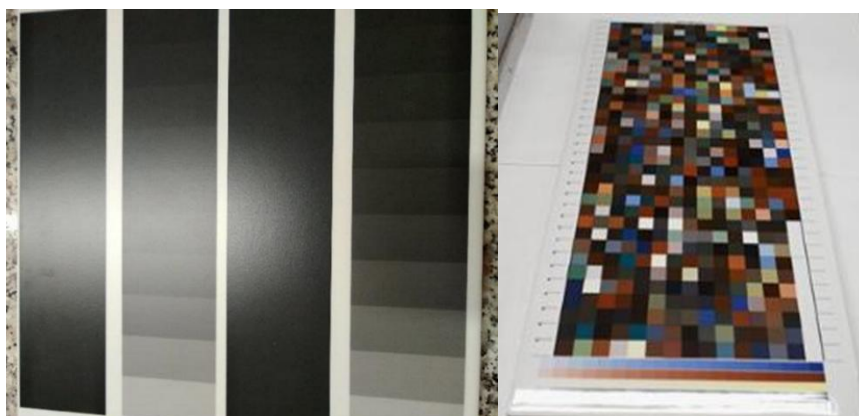


Figure 3. Black printed pattern. Colour garmout

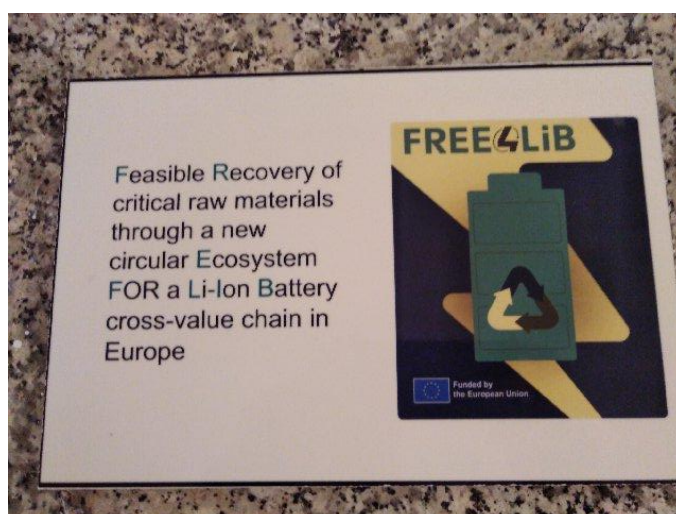


Figure 4. Printed image

Results achieved show the viability to use black mass from direct cathode with Ni/Mn/Co in ceramic pigments scaled up to 1 kg of pigment in industrial gas furnace. The pigment is suitable for processing into inkjet inks. The use of recycled materials will improve the environmental impact on supply mainly for NiO coming from China and CoO from Congo. Considering a 15 Tn /month production and average 20 grCO₂ /TN m3 maritime transport already 190 TN year of CO₂ are saved.

In WP4 S3 BM06 received from CSIC was used also for pigment synthesis following same approach. Table 4 shows the composition of S3BM06. This material was selected being the most restrictive in chemical composition. Pigment was prepared as above replacing 100% of NiO

Table 4. Analysis of S3 BM06

Reference	Metals	Type of Salt	Li	Ni	Mn	Co
S3 BM06	Ni-MN	Oxychloride	0.82	29.8	8.53	0.41



Figure 5. pigment application Matt glaze (VNK) gloss (cristalina). pigment powder

Below in figure 6 the XRD shows same pattern for the standard (red) and the new pigment (black)

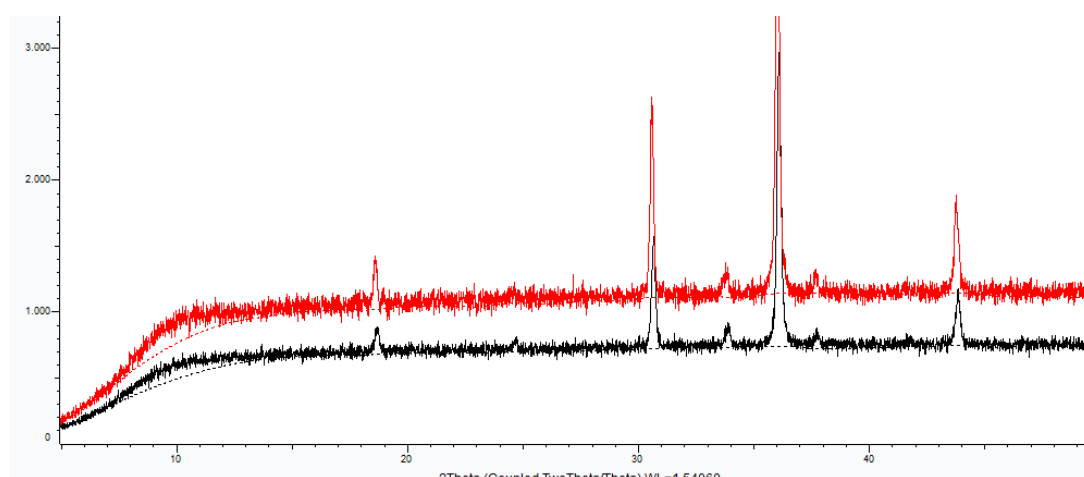


Figure 6. XRD for pigments

The shrinkage of new pigment is 3 times greater, and also the loss of ignition, due to organic content.. Hardness is similar to reference, with the same milling, we obtain analogous particle sizes. The same applies to colorimetry, similar values as shown in table 5 below. They have similar tendencies in both matte (VNK) and gloss (CRISTALINA) glazes.

Table 5. Performance

Ref	Loss	L	A	B	DL M	DA M	DB M	DL C	DA C	DB C	oH	Con- duc- tivity mS/m	CrVI ppm
limit					37,58	0,6	1,11	29,24	0,82	1,12	8,92	286,7	116,56
83968 std	13%	38,47	0,05	0,88	1,92	0,28	0,06	0,99	0,18	0,07	7,007	57,1	<1
83968/NMC4/1	32%	39,33	0,17	0,66	2,29	0,31	0,06	0,83	0,23	0,11	7,35	58,1	<1

It can be concluded from the test that S3 BM06 is valid for pigments.

4.2 Recovery of metal oxides for frits.

Ceramic frits are basic materials for the manufacture of enamels, as well as for digital application with application temperatures between 1,140 and 1,180 °C on ceramic substrate. Frits are used in other fields such as glass decoration and sheet metal enamelling, with working temperatures of 700 and 820 °C. Ceramic frits are glass-based systems based on oxides such as SiO₂, Al₂O₃, Li₂O, Na₂O, K₂O, CaO, MgO, TiO₂, ZrO₂, BaO, CeO₂, B₂O₃, ZnO, B₂O₃ and in the case of enamel frits, adding CoO, NiO and MnO₂ as adhesion promoters. Frits are obtained by mixing raw materials and melting them between 1,200 and 1,500 °C.

WP3 and initial results described in D3.7 showed the potential in frits using initial material CP021 from Cartif. In terms of upscaling diverse materials were available in larger quantities within WP4.

- CP021 Black mass NiCoMn from Cartif, by direct delamination
- Black mass from FIWKS.
- Precursors, carbonates, oxalates and chlorides from CSIC

Within WP4 CP021 was selected for upscaling novel cathode materials and ceramic pigments. The use of precursors from CSIC BM from FIWKS were used for ceramic frits. The table 6 below provide insight in used frits as matrix.

Table 6. Composition of frit

	FR4EFV1	FR4EFV2
SiO ₂ + Al ₂ O ₃	52	70
B ₂ O ₃	17	6
CaO+MgO+BaO	5	3
TiO ₂ + CeO+ZrO ₂	9	4

Na₂O+K₂O	12	11
Li₂O	1	1
MnO₂	1	1
CuO	0	
CoO	1	2
NiO	2	2

Table 7 below shows the characteristic point of frits, measured with hot stage microscope. Values are similar

Table 7. Characteristic points of frit

	FR4EFV1	FR4EFV2
Sintering point °C	640	646
Softening point °C	694	706
Sphere point °C	756	831
1/2 sphere point °C	792	878
1/3 sphere -flow point °C	828	920

Material from FRAUNHOFER IWKS was used as NiO source. 500 gr of frit was prepared. Frit technology melting is based on mixing of raw material, melting in crucibles at 1300 °C at laboratory scale between 300gr to 500gr, whereas industrial furnaces produce 800 kg/h. Laboratory results are direct scalable. The main problem was the high graphite content that led to reductions of iron from the frit.

Figure 7 below shows the reduced iron and application on steel as enamel. The frit was applied as enamel on steel DC01 EK. As can be seen, the results are bad due to the iron reduction. This reduction is due to high carbon content, showing that this material cannot be used.



Figure 7. Reduced iron. Enamel performance. Left std, right using BM FIWKS

Along WP4 CSIC supplied diverse metal oxide precursors as shown in table 8. Some were tested for active materials and other for frits.

Table 8 Precursors supplied

Reference	Type of oxide	Date	Use
RE04	Ni_Mn-	16-10-2025	
S3BM04	NIMN	25.11.2025	
S0 BM05	Li ₂ CO ₃	25.11.2025	used in frits
S3 BM05	Ni Mn	25.11.2025	used in frits
S1BM06	Li ₂ CO ₃	5-1-2026	
S2 BM06	Ni-Mn-Co	5-1-2026	used in frits
S3 BM06	Ni-MN	5-1-2026	
S4-BM06	Mn-Co	5-1-2026	

Analysis is shown in table 9 and type of precursor

Table 9. Analysis of precursors

Reference	Metals	Type of salt	Li	Ni	Mn	Co
RE04-	Ni_Mn-		0.14	23.8	8.66	0.39
S3.BM04	NiMn		0.14	23.86	8.06	0.69
S0 BM05	Li ₂ CO ₃	carbonate				
S3 BM05	Ni Mn		0.2	22.89	6.22	0.309
S1BM06	Li ₂ CO ₃	Carbonate				
S2 BM06	Ni-Mn-Co	Oxalate	0.6	22.2	13.31	6.37
S3 BM06	Ni-MN	oxichlo-ride	0.82	29.8	8.53	0.41
S4-BM06	Mn-Co	sulphate	0	2	18.88	23.49

Considering the type of precursors, 3 frits were molten. In one S0BM05 Li₂CO₃ was used and in the other S2BM06 and S3 BM06 were used as Ni-Mn-Co source.

The objective was to evaluate replicability in use of diverse precursors for frits. Raw materials were mixed, molten at 1300 °C. The final frit was milled into a slurry with clay and additives and applied on DC01 steel. The steel sample was fired at 810 °C.

Image 8 below shows the enamelled steel DC01 with two frits using S0BM05 and S2BM06. On the fired sample adhesion was measured by impacting a steel ball from 1 m. The image shows also the results showing good adhesion. Slight difference in colour is obtained using S0BM05 but this is not a major problem since Ni/CO ration can be adjusted or a CuCr pigment added



Figure 8. Frits application

In the case of S3 BM06 oxychloride the performance was worst as can be seen in the image 9.



Figure 9. Image of frit application S3BM06

For the frits, the main melting points were measured with a hot stage microscope, being shown in table 10. Type of precursor does not affect the melting performance.

Table 10. Main properties of frits

	FR4EFV1 reference	FR4EFV1 with CP021	FR4EFV3 S0BM05 Li2CO3	FR4EFV5 With S2BM06	FR\$EFV6 with S3 BM06
Sintering point °C	640	640	643	635	642
Softening point° C	694	685	690	680	682
Sphere point °C	756	746	750	745	740
1/2 sphere point °C	792	790	790	781	782
1/3 sphere -flow point °C	828	820	826	815	815

In general, it can be concluded that black mass and precursors can be used for frits depending of impurities. High carbon content is not acceptable, being limit about 5-8 % based on additional trials. Regarding precursors, they can be use in case of lithium carbonate or oxalates. Chlorides do not show good integration.

4.3 Thermoset materials recovery (microwave-assisted by pyrolysis)

Thermoset plastic fractions previously classified in Task 3.5 as non-reprocessable were subjected to microwave (MW)-assisted pyrolysis at the AIMPLAS pilot plant. The objective of this process was to thermally decompose the material into three distinct fractions—solid (char), liquid (pyrolytic oil), and gaseous products—to assess their potential recovery as secondary raw materials.

A series of experimental trials were carried out to optimise key process parameters, including residence time, microwave power, and target temperature, in order to maximise conversion efficiency and control the composition of the resulting fractions. The gas and liquid outputs were subsequently analysed by gas chromatography (GC) to characterise volatile and semi volatile organic species while the solid residue was evaluated for elemental composition and potential valorisation routes.

Based on the obtained results, a preliminary assessment of potential reuse pathways for each fraction was conducted, taking into account their chemical nature, purity, and market relevance.

This activity aims to demonstrate innovative and flexible thermal recycling routes capable of adapting to the heterogeneous waste streams generated during the treatment of end-of-life (EoL) and production scrap from lithium-ion batteries, with a specific focus on the plastic fraction. The microwave-assisted pyrolysis process provides an alternative recycling pathway for thermoset materials, which cannot be mechanically reprocessed, contributing to the broader objectives of circularity and resource recovery within the FREE4LiB framework.

4.3.1 Experimental approach.

The thermoset material fractions, provided by the partner Fraunhofer, consisted of flexible greyish films (less than 3 mm thickness) recovered from end-of-life (EoL) battery packs (Figure 10). The films displayed two distinct surface morphologies: continuous shiny white areas, indicative of the base polymer substrate, and opaque, powdery beige regions, suggestive of a coating layer. Additionally, local dark-grey opaque inclusions were present, likely corresponding to conductive fillers or degraded residues.





Figure 10. Thermoset sample recovered from EoL battery packs.

An initial characterization was performed to determine the composition and thermal behaviour of the material prior to pyrolysis. Techniques employed included:

- Fourier Transform Infrared Spectroscopy (FTIR) to identify polymer families and coatings.
- Differential Scanning Calorimetry (DSC) to assess melting/crystallisation behaviour and derive decomposition onset temperature.
- Thermogravimetric Analysis (TGA) to measure decomposition profile, residual mass and enthalpy changes.

These analyses allowed defining the thermal stability window of the sample and helped select appropriate operating temperatures for the microwave-assisted process. After characterization, the samples were subjected to Microwave-assisted pyrolysis (MAP), directly without any additional pre-treatment; MAP is a thermo-chemical conversion technology which uses microwave electromagnetic fields to heat materials via dielectric heating (dipole rotation and ion conduction) rather than by conduction from external heating surfaces¹. This mode of heating enables rapid internal heating, more uniform temperature distribution within the feedstock, and improved energy efficiency compared to conventional pyrolysis.

In plastics recycling research, MAP has demonstrated advantages including higher heating rates, lower tar and char formation, enhanced selectivity to target product fractions (e.g., hydrogen-rich gas or olefins), and reduced process residence times².

¹ Yang, C., Shang, H., Li, J., Fan, X., Sun, J., & Duan, A. (2023). A Review on the Microwave-Assisted Pyrolysis of Waste Plastics. *Processes*, 11(5), 1487. <https://doi.org/10.3390/pr11051487>

² Psenovschi, G., Calinescu, I., Fiti, A., Chisega-Negrila, C.-G., Ionascu, S.-L., & Barbes, L. (2025). Microwave-Assisted Pyrolysis of Polyethylene and Polypropylene from End-

It is particularly suited to heterogeneous waste streams, such as thermoset fractions, where rapid, uniform heating can help overcome thermal inertia and minimise local overheating or incomplete decomposition.

For the operating procedure, the films were processed in a laboratory-scale microwave pyrolysis reactor under inert (N_2) atmosphere, incorporating in-situ activated carbon (AC) adsorbent to capture any potentially released halogenated volatile species. Key operating parameters involved:

- Target process temperature: 600 °C
- Residence time: 90 min
- Cooling time: 60 min
- AC to sample mass ratio: 1:1
- Atmosphere: N_2 , endogenous pressure



Figure 11. Microwave- assisted by pyrolysis set up.

The initial sample mass was 5.08 g. Following microwave-assisted pyrolysis, the process generated the three characteristic product streams: a gaseous fraction consisting of non-condensable volatiles and light hydrocarbons, a liquid pyrolytic oil composed of condensable organic compounds, and a solid char residue containing carbonaceous and inorganic remnants. The corresponding mass fractions obtained are presented in (table 11;**Error! No se encuentra el origen de la referencia.**). Note these values represent only the material originating from the thermoset sample itself. An activated carbon adsorbent was introduced in situ inside the reactor to capture volatile species; consequently, the mass balance reported excludes both the mass of the adsorbent and any compounds retained on its surface during processing.

of-Life Vehicles: Hydrogen Production and Energy Valorization. Sustainability, 17(13), 6196. <https://doi.org/10.3390/su17136196>



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Table 11. Pyrolysis mass balance.

	Char/Ashes	Liquids/waxes	Gases
Obtained weight (g)	1.9	0.08	3.1
Obtained weight (wt. %)	37.4 %	1.6 %	61 %

This distribution is characteristic of highly crosslinked thermoset polymer systems, where the three-dimensional network restricts depolymerisation into condensable intermediates and instead favours chain scission pathways producing light permanent gases (CO, CO₂, small hydrocarbons) under high-temperature inert conditions.

The relatively high char yield (37.4 wt.%) further corroborates the presence of inorganic fillers, pigments-like residues, as well as the formation of carbonaceous structures typical of thermosets that do not melt and instead undergo aromatic condensation and carbonisation during pyrolysis. In addition, the very low liquid yield (1.6 wt.%) indicates that only a minor fraction of the material is converted into condensable hydrocarbons or waxes, confirming limited potential for recovering valuable pyrolytic oils from this waste stream. This behaviour aligns with the expected degradation profile of polyolefin-based films containing multilayer coatings or inorganic charge, where the organic fraction is insufficient to generate stable long-chain condensates.

Overall, the results demonstrate that the selected thermoset fraction is gas-rich and char-forming, with poor oil recovery potential, which has direct implications for downstream valorisation strategies: the gaseous fraction may be suitable as process fuel, while the solid char—depending on its composition—may be assessed for use in adsorbents, fillers, or energy applications, as explored in the subsequent sections of the deliverable.

4.3.2 Materials characterization.

The preliminary characterisation of the initial sample (Figure 10) using FTIR spectroscopy aimed to identify the base polymer and detect the presence of coatings, inorganic fillers, or other functional layers. The analysis confirmed that the substrate corresponds to a polyolefin matrix, exhibiting a characteristic polyethylene (PE) spectral profile. In addition, several absorption bands were detected that are not typically associated with polyolefins, suggesting the presence of non-polyolefin components or potentially halogen-containing functionalities (Figure 13), which may influence decomposition behaviour during pyrolysis.



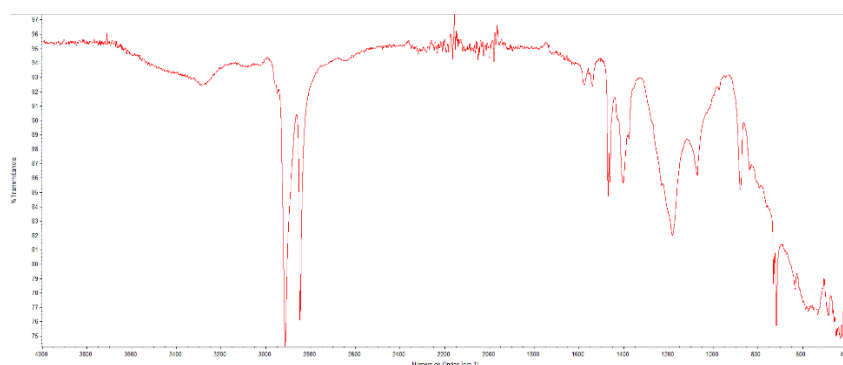


Figure 12. FTIR spectral profile (polyolefin-like fingerprint)



Figure 13. FTIR spectral profile (halogen-like fingerprint)

Complementarily, the DSC (Figure 13) and TGA (Figure 14) analyses confirmed that significant volatilisation of the sample occurs only above 500 °C, consistent with the thermal degradation profile of polyolefin-based materials. The DSC thermogram showed an onset of melting above 126 °C, which aligns with the characteristic melting range of polyethylene-rich systems, as previously indicated by the FTIR results.

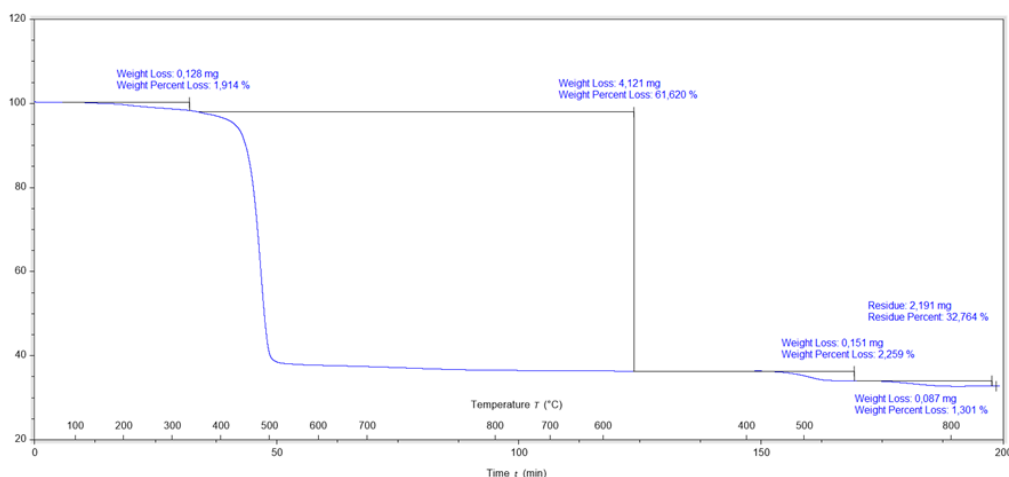


Figure 14. TGA analysis obtained for film sample.

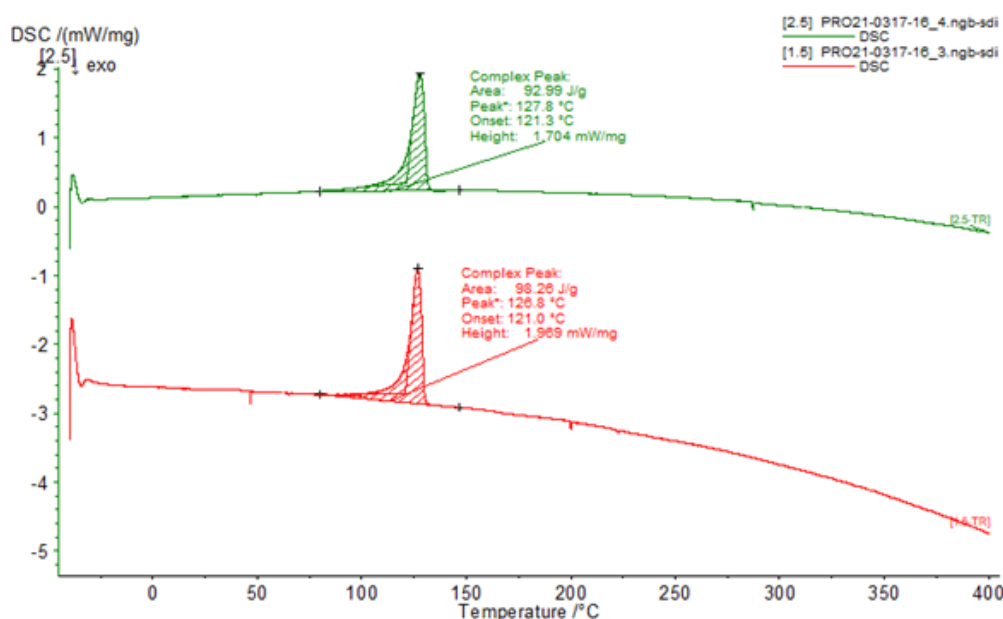


Figure 15. DSC analysis obtained for film sample.

An integrated analysis of the gasified sample was performed using Gas Chromatography–Mass Spectrometry (GC–MS) to characterise the composition of the condensable fraction (pyrolytic liquids/waxes and semi volatiles) and to assess its correlation with the thermal degradation behaviour of the material. Since direct collection of the gaseous stream is not feasible in the microwave reactor configuration used in this study, a GC–MS simulation was carried out to provide an indicative profile of the volatile/semi volatile compounds expected during pyrolysis.

Complementarily, the solid residue (char/ashes) was analysed for halogen content in order to verify whether the minor bands detected in the FTIR spectrum corresponded to halogen-containing species. This analysis also aimed to determine whether the in-situ activated carbon adsorbent effectively retained potential halogenated degradation products or, conversely, whether these species were released into the volatile fraction. This distinction is crucial from a process-operation standpoint, as halogen-containing volatiles can lead to equipment corrosion and are generally undesirable in pyrolysis systems. The combined GC–MS results are summarised in table 12:

Table 12. GC–MS results, volatiles and semi volatiles fractions

Retention time	Substance	CAS	SI	RSI	mg/kg sample
1.558	Acetaldehyde	75-07-0	781	791	32,022
1.647	Ethanol	64-17-5	908	914	37,753
1.738	Possible Butane	106-97-8	791	845	21,478
1.841	2-Propenenitrile	107-13-1	918	951	33,149

1.973	1-Propanol	71-23-8	741	772	3,216
2.038	Methacrolein or isomer C ₄ H ₆ O	78-58-3	691	769	2,564
2.157	Butanal	123-72-8	782	848	3,542
2.170	Butanal	123-72-8	853	890	2,247
2.201	2-Butanone	78-93-3	823	896	6,371
2.327	Ethane, (methylthio)- / 2-Propanethiol	624-89-5 / 75-33-2	627	916	1,355
2.565	3-Hexanol / Amylene hydrate	623-37-0 / 75-85-4	652	766	0,647
2.698	2-Butenal, (E)- / Furan, 2,5-dihydro-	123-73-9 / 1708-29-8	745	885	0,855
2.820	Benzene	71-43-2	910	946	11,947
2.905	2H-Pyran, 3,4-dihydro- / 1,3-Cyclopentanediol, trans- or isomer	110-87-2 / 16326-98-0	695	735	0,696
3.174	2-Pentanone	107-87-9	826	850	1,553
3.323	Cyclopentanol	96-41-3	803	833	1,574
3.436	Carbonic acid, ethyl-, methyl ester or isomer	623-53-0	831	832	2,762
3.585	2,4-Dimethylfuran or isomer	3710-43-8	831	856	0,876
4.146	Disulfide, dimethyl	624-92-0	728	817	0,640
4.585	Unknown (possible aromatic compound)	-	-	-	0,662
4.980	3-Hexanone	589-38-8	777	873	0,630
5.058	1-Octene	111-66-0	799	830	0,899
5.265	Hexanal	66-25-1	787	867	1,021
5.714	Cyclotrisiloxane, hexamethyl-	541-05-9	942	942	3,208
9.146	Cyclotetrasiloxane, octamethyl-	556-67-2	932	933	13,599
9.700	1-Hexanol, 2-ethyl-	104-76-7	800	875	0,708
10.197	Linear or branched alkane	-	-	-	0,619
10.840	Benzene, (1,1-dimethylpropyl)-	2049-95-8	911	919	6,575
11.159	Neomenthol acetate or isomer	54845-18-0	569	707	0,598
12.466	Dodecane	112-40-3	798	832	0,659
13.397	Linear or branched alkane	-	-	-	0,685
13.639	Linear or branched alkane	-	-	-	0,865

13.758	Linear or branched alkane	-	-	-	0,593
14.275	Linear or branched alkane	-	-	-	0,759

The GC–MS analysis revealed a chemically complex volatile fraction dominated by oxygenated light compounds, short-chain hydrocarbons, aromatic species, and volatile siloxanes. This profile confirms that the recovered film is not a simple polyolefin sheet but a multilayer material incorporating surface coatings and silicon-based additives.

The most abundant compounds detected—acetaldehyde, ethanol, butane, 2-propenenitrile, benzene, and cyclic siloxanes such as D3 and D4—align closely with the degradation patterns previously established by FTIR, DSC, and TGA:

- The presence of aldehydes, ketones, and small alcohols corresponds to the early thermal events observed below 350 °C in TGA and reflects decomposition of surface coatings, adhesive residues, or minor functional additives identified in FTIR.
- Light alkanes and alkenes (e.g., butane, 1-octene, C10–C14 linear/branched hydrocarbons) are characteristic products of polyethylene chain scission, confirming that the matrix is polyolefin-based, in agreement with FTIR fingerprints.
- Aromatic species such as benzene and alkyl-substituted benzenes indicate secondary cracking at elevated temperatures (~600 °C), consistent with the high proportion of gaseous products (≈61 wt.%).
- The detection of cyclic siloxanes (D3, D4) is particularly relevant: their presence reveals silicon-rich additives or coatings on the original film, which matches the white/beige powdery regions observed visually. Their partial volatilisation explains both the significant silicon content in the gas fraction and the inorganic residues found in the solid char (≈37 wt.%).

Taken together, the GC–MS results confirm that the sample behaves as a heterogeneous composite, where a polyethylene substrate is combined with silicon-containing functional layers. This heterogeneity leads to a pyrolysis profile dominated by volatile products, with limited liquid yield (≈1.6 wt.%). From a valorisation standpoint, the gas composition suggests potential for energetic recovery, although aromatics and siloxanes would require downstream cleaning or *scrubbing* to avoid equipment corrosion and emissions issues.

Overall, these findings suggest the need for pre-sorting, de-coating, or surface cleaning strategies when treating coated thermoset or thermoplastic films in future recycling workflows to improve process efficiency and product quality.

Regarding the analysis of the solid fraction, the sample was evaluated following the DIN EN 15408:2011-05 standard, after first determining its moisture content to ensure compliance with the method's requirements. The results in wt.% are presented in 13:

Table 13. Content of fluorine results

	Test method	RL*	Results
Dry substance in %	DIN EN ISO 21660-3:2021-06	0,1	99,1**
Sample preparation	DIN EN ISO 21646: 2022-09		

Parameter	Test method	RL*	Results
Fluorine in mg/kg	DIN EN 15408:2011-05	4	10000

* Reporting limit

**Result expressed on original (non-dried) material

Table 14. Content of fluorine results

The analysis revealed a notably high fluorine concentration in the solid fraction ($\approx 10,000$ mg/kg), indicating that a significant portion of the halogens present in the original film was retained by the char. This behaviour is consistent with the presence of fluorinated species or fluorinated surface coatings—most plausibly PTFE-type (Teflon-like) layers or species inherited from other battery components in contact—previously suggested by FTIR analysis and by the visual identification of powdery white/beige areas on the film.

Importantly, fluorine was not detected in the semi-volatile or volatile phases, suggesting that the in-situ activated carbon used during microwave pyrolysis effectively adsorbed halogenated species, preventing their transfer into the gaseous stream. From an operational perspective, this is critical: halogens in the vapour phase are highly undesirable, as they can corrode reactor components and compromise downstream energy-recovery systems.

Although the presence of fluorinated coatings makes the material intrinsically less suitable for pyrolysis-based recycling, the observed retention of fluorine in the solid adsorbent demonstrates that its impact can be mitigated through appropriate selection and dosing of sorbents. This highlights a potential pathway for improving the treatment of halogen-containing thermoset or coated polyolefin components in future process optimisation.

4.3.3 Assessment of potential reuse pathways.

The pyrolysis results show that the material breaks down mainly into gases (≈ 61 wt.%), while generating a significant amount of solid residue (≈ 37 wt.%) and only a very small quantity of liquid products (≈ 1.6 wt.%). The gas stream—composed of light hydrocarbons, oxygenated compounds, aromatics and volatile siloxanes—has limited value as a chemical feedstock, but it could potentially be used as a fuel inside controlled waste-to-energy systems. However, siloxanes would need to be removed first, as they form abrasive silica particles during combustion.

By contrast, the solid residue offers more realistic opportunities for reuse. The char captures most of the inorganic and fluorinated components of the original material, including a very high fluorine content ($\sim 10,000$ mg/kg). This means the char could be considered for low-grade applications such as adsorbent materials, fillers in construction products, or energy recovery—but only after appropriate stabilization or purification, due to the presence of halogens. The very low liquid yield and its composition indicate it has no practical value for recycling. Overall, the material shows limited potential for high-quality recovery by pyrolysis, but the solid and gas fractions may still be usable if properly treated (see Figure 16):

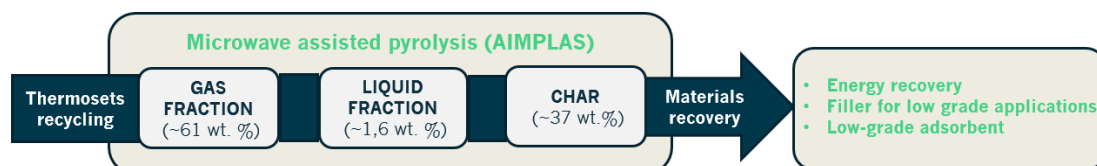


Figure 16. Workflow for ST4.11.2. Thermal recycling by microwave pyrolysis (AIMPLAS)

5. Conclusions

Deliverable 4.8 summarizes the use of recycled precursors in other fields to a upscaled extent.

In the case of ceramic pigments Task 4.11 has validated the use of recycled precursor CP021 for pigments and defined conditions for successful integration of black mass and precursors in frits, showing the viability using 2 different recycled precursors. Use of CP021 is valid for frits with no modification of the melting performance.

In terms of precursors salts, recycled Li_2CO_3 from CSIC is valid. Precursors can be used for frits depending of impurities. High carbon content is not acceptable, being limit about 5-8 % based on additional trials. Regarding precursors oxalates are valid while chlorides do not show good integration.

Microwave-assisted pyrolysis can thermally degrade thermoset-containing battery plastics, but the resulting fractions offer limited valorisation potential without further technological optimisation. The findings reinforce the need for alternative recycling approaches (e.g., chemical depolymerisation, specialised de-coating processes, or incineration with energy recovery) for similar multi-layer or coated thermoset films within the EV battery stream.