

# Up-scale Pyrolysis of Selected Aarhus River Plastic

Report

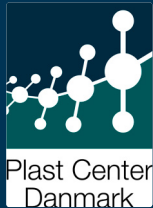
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Report on Identification of polymer types and recycling possibilities in river-collected ocean-bound plastic

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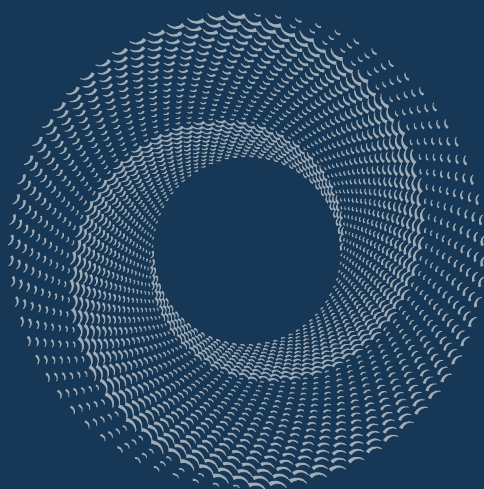
**South Baltic**



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# 1. Introduction





# 1. Introduction

In connection with the Circular Ocean-bound Plastic (COP) project, pyrolysis was investigated as a possible chemical recycling route for selected fractions of ocean-bound plastic collected from Aarhus River. Based on previous material identification and sorting activities, polypropylene (PP) and polyethylene (PE) were selected as relevant polymer fractions for pyrolysis testing. These polymers were chosen because they were present in significant amounts in the collected OBP stream and because polyolefin-rich fractions are generally among the most relevant plastic types for pyrolysis.

In total, six pyrolysis reactions were performed. Four reactions were carried out on polypropylene samples and two reactions were carried out on polyethylene samples. The PP test series consisted of two contaminated Aarhus River PP samples, one washed Aarhus River PP sample and one virgin PP reference. The contaminated samples were included to evaluate the behaviour and repeatability of untreated OBP material, while the washed and virgin samples were used to assess the influence of washing and to provide a clean reference for comparison.

The PE test series included one pyrolysis reaction on contaminated PE collected from Aarhus River and one reaction on virgin PE. The contaminated PE fraction from Aarhus River consisted of approximately 60% low-density polyethylene (LDPE) and 40% high-density polyethylene (HDPE). A virgin PE reference blend with the same composition, 60% LDPE and 40% HDPE, was pyrolysed for comparison. This made it possible to evaluate whether contamination from the river-collected PE fraction influenced the pyrolysis products compared with a clean reference material of similar polymer composition.

The pyrolysis process produced three main product fractions: liquid oil/wax, gas, and solid residue/char. The oil/wax products were investigated through density determination, total acid number determination, Fourier Transform Infrared Spectroscopy (FTIR), and Gas Chromatography coupled with Mass Spectrometry (GC-MS). FTIR was used as a qualitative method to evaluate the overall chemical structure and main functional groups present in both the oil/wax products and the solid residue/char. GC-MS was used to identify organic compounds present in the oil/wax products.

The solid residue/char was further investigated using X-Ray Fluorescence (XRF) to determine elemental composition and Thermogravimetric Analysis (TGA) to evaluate thermal degradation behaviour and residual ash/inorganic content.

By comparing contaminated Aarhus River PP, washed Aarhus River PP, and virgin PP, the study

evaluates the influence of contamination and washing on pyrolysis products from polypropylene.

The results are used to assess whether pyrolysis can be a relevant complementary recycling route for selected OBP fractions that are difficult to recycle mechanically.

## Samples

In total, six samples were included in the pyrolysis study. To make the presentation of the results clearer, the samples are referred to as Sample 1–Sample 6 throughout the report. The sample names, material type, condition, and purpose are shown in Table 1.

Table 1 Overview of samples used in the report

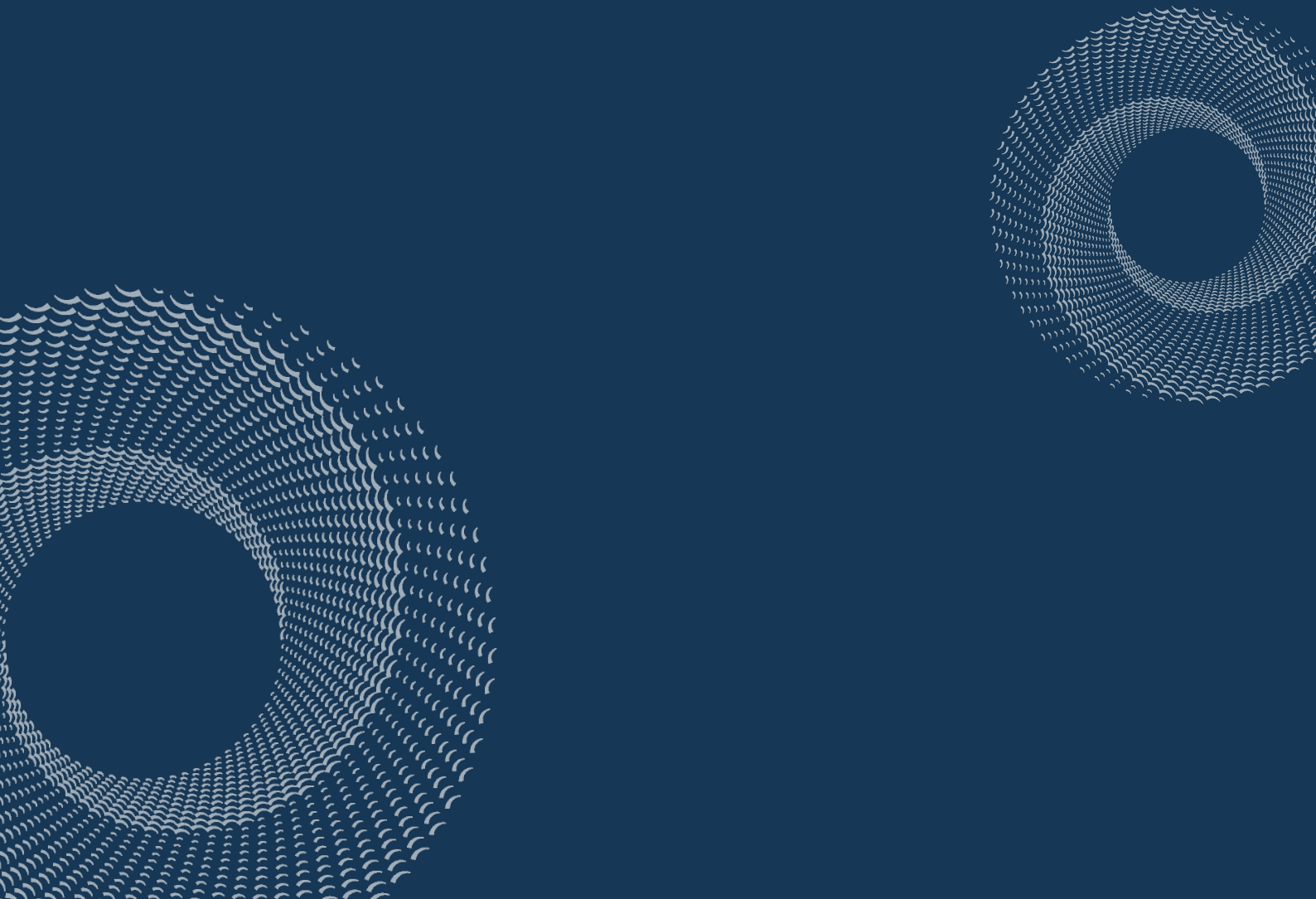
| Sample   | Material              | Condition                            | Purpose                                                 |
|----------|-----------------------|--------------------------------------|---------------------------------------------------------|
| Sample 1 | Aarhus River PP       | Dirty/untreated                      | Evaluate pyrolysis of contaminated PP                   |
| Sample 2 | Aarhus River PP       | Dirty/untreated                      | Repeat contaminated PP pyrolysis                        |
| Sample 3 | Virgin PP             | Clean reference                      | Reference for PP pyrolysis                              |
| Sample 4 | Aarhus River PP       | Washed                               | Evaluate the effect of washing on PP pyrolysis products |
| Sample 5 | Aarhus River PE blend | Dirty/untreated                      | Evaluate pyrolysis of contaminated PE                   |
| Sample 6 | Virgin PE blend       | Clean reference, 60% LDPE / 40% HDPE | Reference for PE pyrolysis                              |





2.

## Pre-treatment of selected OBP fractions





## 2. Pre-treatment of selected OBP fractions

Before pyrolysis, the selected PP and PE fractions were manually sorted from the ocean-bound plastic material collected from Aarhus River. The selection was based on previous material identification and sorting activities, where polypropylene (PP) and polyethylene (PE) were identified as relevant polyolefin fractions for chemical recycling by pyrolysis.

The river-collected material contained visible contamination, such as dirt, organic residues, biofilm, labels, pigments, and other non-polymeric material attached to the plastic surface. In order to evaluate the influence of contamination on the pyrolysis process and products, selected samples were pyrolysed in their dirty/untreated condition.

Examples of the selected river-collected plastic fractions before pyrolysis are shown in Figure 1.



Fig. 1 Selected PP (a) and PE (b) fractions from Aarhus River before pyrolysis. The materials contained visible surface contamination, labels, pigments and other non-polymeric residues.

Samples 1 and 2 consisted of contaminated Aarhus River PP and were used without washing before pyrolysis. The material was ground before being introduced into the pyrolysis reactor. These two samples were included to evaluate the behaviour of untreated PP from the OBP stream and to assess repeatability between two contaminated PP pyrolysis reactions.

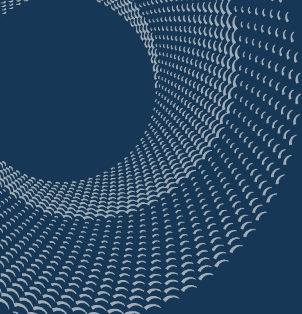
Sample 3, the virgin PP reference, was supplied in pellet form and was used without further size reduction.

Sample 4 consisted of Aarhus River PP that was washed and subsequently ground before pyrolysis. The washing step was performed to remove visible surface contamination and to evaluate whether cleaning the material influenced the composition of the oil/wax product and the solid residue/char. The washed PP sample was compared with both the dirty/untreated PP samples and the virgin PP reference.

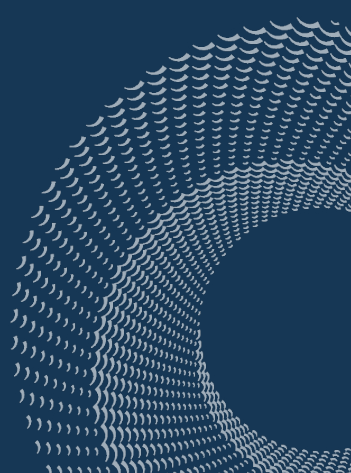
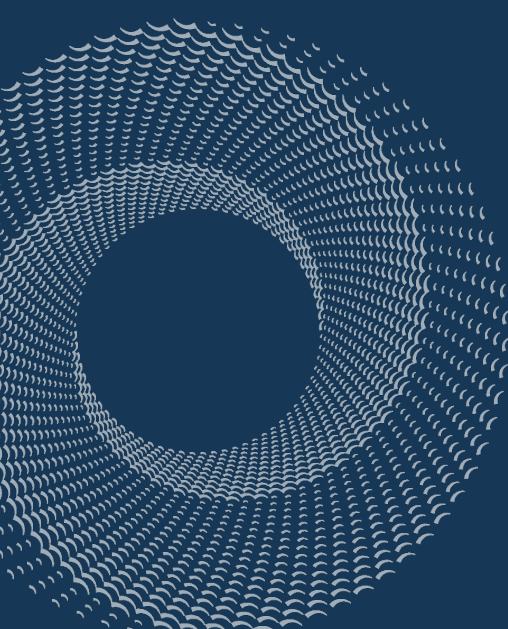
Sample 5 consisted of contaminated Aarhus River PE and was used in its dirty/untreated condition. The PE fraction consisted of approximately 60% LDPE and 40% HDPE.

Sample 6 was prepared as a clean virgin PE reference blend with the same composition, 60% LDPE and 40% HDPE. The virgin PE materials were supplied in pellet form and were used without further size reduction. Virgin PP and virgin PE reference materials were included to provide clean baseline samples.

These reference samples made it possible to evaluate whether differences in the pyrolysis products were mainly related to polymer type, contamination, washing, or the use of river-collected material.



# 3. Pyrolysis process





### 3. Pyrolysis process

The selected PP and PE fractions were processed by batch pyrolysis. During the process, the plastic material was heated in an oxygen-free atmosphere under a continuous flow of nitrogen. The nitrogen displaced oxygen from the reactor and maintained an inert atmosphere, preventing combustion and allowing the polymer chains to decompose thermally. The process produced three main product fractions: condensable oil/wax, non-condensable gas, and solid residue/char.

The pyrolysis setup consisted of a heated reactor section and a condensation and product collection system. The plastic sample was placed in the reactor and heated to promote thermal cracking of the polymer material. The vapours formed during pyrolysis were transferred from the reactor to the condensation system, where the condensable fraction was collected as oil/wax. The non-condensable fraction was not collected directly and is therefore included in the calculated gas fraction in the mass balance. After cooling, the remaining solid residue/char was collected from the reactor. The pyrolysis setup used in the experiments is shown in Figure 2.

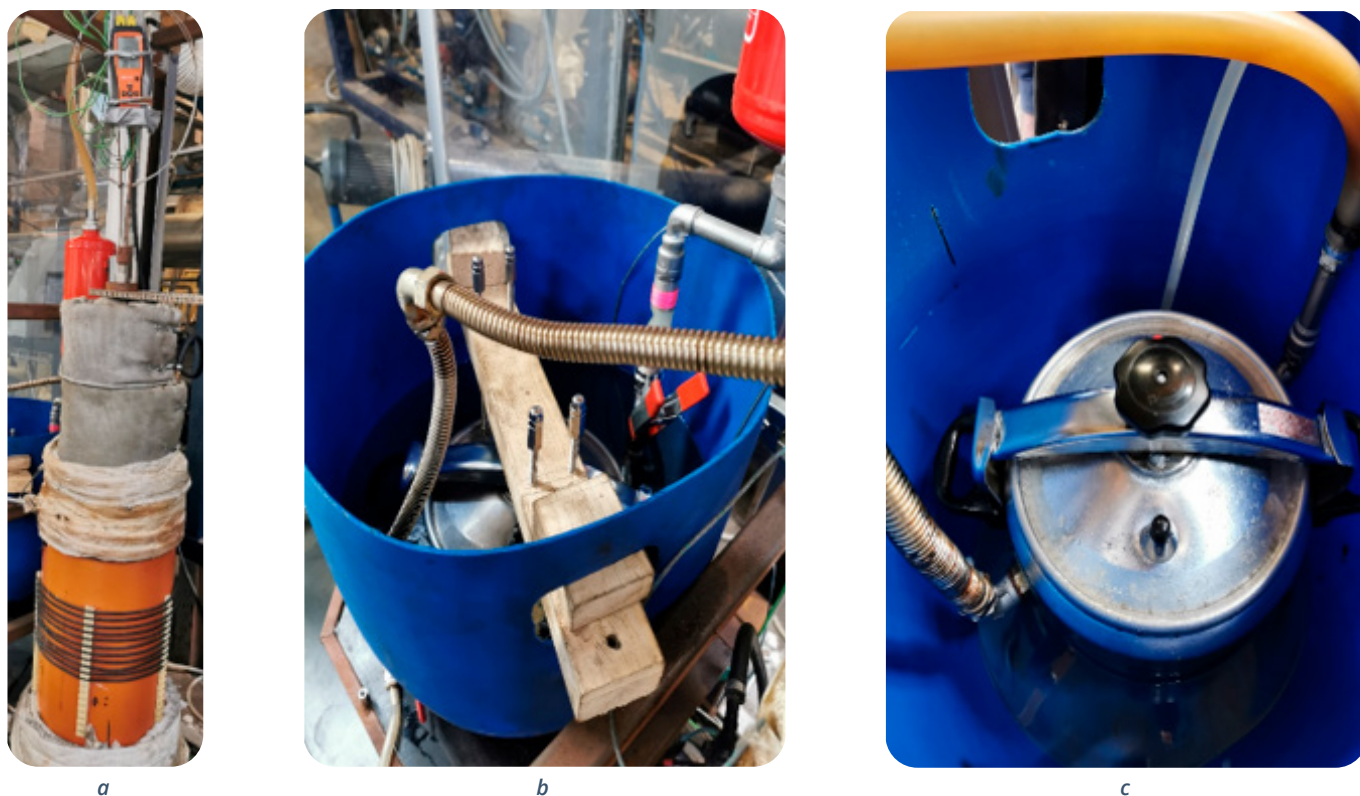


Fig. 2 Pyrolysis setup used for the conversion of selected PP and PE fractions. a) Reactor/heating section, b) condensation and product collection system, and c) collection vessel for condensed oil/wax product.

The condensable fraction was collected as one fraction composed of oil and wax. Depending on the sample and product composition, the collected product appeared either as a liquid oil or as a more

viscous/waxy material after cooling, as shown in Figure 3.



Fig. 3 Examples of condensed oil/wax products collected after pyrolysis. a) Liquid oil/wax fraction during collection and b) heavier wax-like oil product after cooling.

The pyrolysis setup was monitored using several temperature measurements, as shown in Figure 4. The control panel was used to monitor the heating zones, reactor tube, condenser outlet and cooling water temperature. The heating section included separate temperature control for the upper, middle and lower parts of the reactor. In addition, internal temperature measurements were followed during the process to monitor the temperature development inside the reactor. This allowed both the pyrolysis process and the condensation step to be monitored during operation.



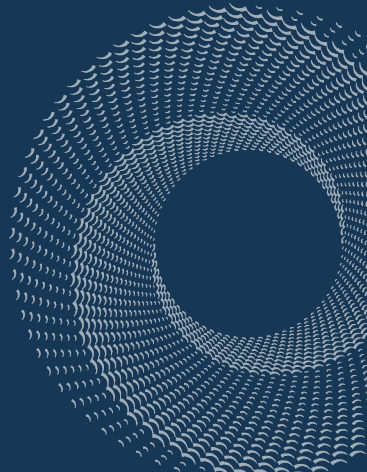
Fig. 4 Temperature monitoring during pyrolysis. a) Temperature control panel for the heating zones, reactor tube, condenser outlet and cooling water, and b) internal temperature monitoring during the pyrolysis process.

Inside the reactor, a screw-shaped mixing element was used to support movement and mixing of the plastic material during heating, as shown in Figure 5. This helped distribute the material in the heated zone and supported more uniform thermal exposure during the pyrolysis process.

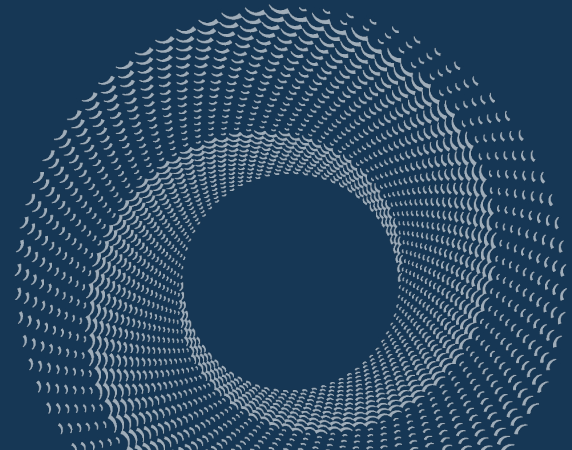
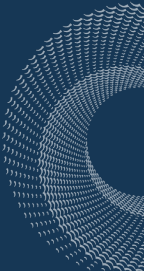
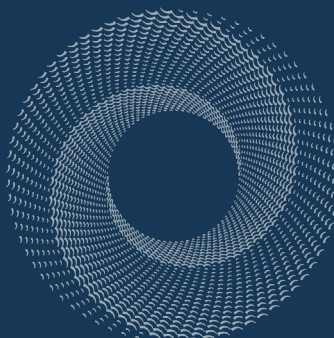


Fig. 5 Internal mixing element of the batch pyrolysis reactor. The screw-shaped mixing element was used to move and mix the plastic material during heating.





# 4. Product yield and mass balance





## 4. Product yield and mass balance

The product yield and mass balance were determined for the six pyrolysis reactions. The input mass, collected oil/wax mass and char mass were recorded after each pyrolysis experiment. The gas fraction was calculated by difference between the input mass and the collected oil/wax and char fractions.

The oil/wax yield, char yield and gas fraction were calculated as percentages of the input mass. The input mass was normalised to 100% for each sample. Since the gas phase was not collected or weighed directly, the gas fraction includes non-condensable gases, volatile compounds not collected in the condensation system and possible experimental losses. The detailed mass balance with measured masses is included in Appendix A.

Table 2 Product yield distribution from pyrolysis Samples 1–6.

| Sample   | Input (%) | Oil/wax yield (%) | Char yield (%) | Gas (%) |
|----------|-----------|-------------------|----------------|---------|
| Sample 1 | 100       | 79.5              | 0.4            | 20.1    |
| Sample 2 | 100       | 78.9              | 1.0            | 20.1    |
| Sample 3 | 100       | 66.4              | 0.2            | 33.4    |
| Sample 4 | 100       | 73.1              | 0.1            | 26.8    |
| Sample 5 | 100       | 37.6              | 1.5            | 60.9    |
| Sample 6 | 100       | 86.2              | 0.2            | 13.6    |

The results show that the oil/wax fraction was the main collected product for most samples. For the PP samples, Samples 1–4, the oil/wax yield ranged from 66.4% to 79.5%. Samples 1 and 2, both contaminated Aarhus River PP, showed very similar oil/wax yields of 79.5% and 78.9%, respectively. This indicates good repeatability between the two contaminated PP pyrolysis reactions. Sample 4, washed Aarhus River PP, produced an oil/wax yield of 73.1%, while Sample 3, virgin PP, produced an oil/wax yield of 66.4%.

The char yield was low for all PP samples, ranging from 0.1% to 1.0%. Sample 2 showed the highest char yield among the PP samples, while Sample 4 showed the lowest char yield. The relatively low char formation indicates that most of the PP material was converted into oil/wax and gas fractions during pyrolysis.

For the PE samples, a clear difference was observed between contaminated Aarhus River PE and virgin PE. Sample 5, contaminated PE, produced the lowest oil/wax yield, at 37.6%, and the highest gas fraction, at 60.9%. In contrast, Sample 6, virgin PE, produced the highest oil/wax yield of all samples, at 86.2%, and the lowest gas fraction, at 13.6%. This indicates that the contaminated PE sample behaved differently from the virgin PE reference during pyrolysis.

Overall, the mass balance results show that product distribution depended on polymer type and sample condition. The PP samples mainly produced oil/wax, with relatively low char formation. The virgin PE sample also produced a high oil/wax yield, while the contaminated PE sample showed a much higher gas fraction and lower oil/wax yield. This suggests that contamination, material composition and process behaviour may influence the distribution between oil/wax, char and gas fractions.

The collected oil/wax and char products from the six pyrolysis reactions are shown in Figure 6 and Figure 7.

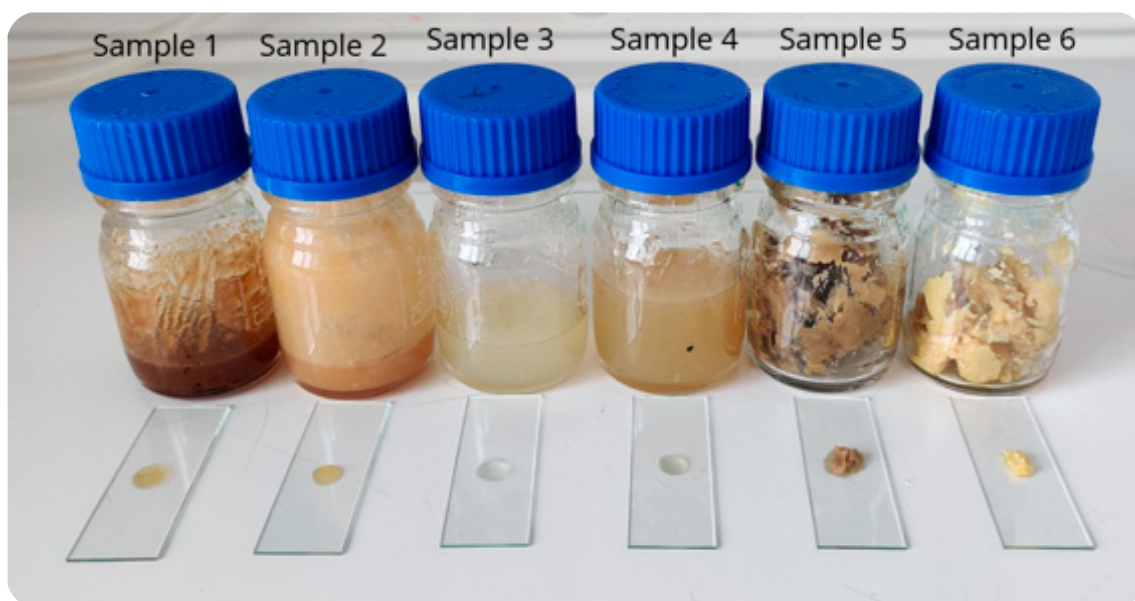


Fig. 6 Oil/wax products collected from pyrolysis of Samples 1–6. The products showed visible differences in colour and physical appearance, ranging from lighter liquid-like fractions to darker and more wax-like products.

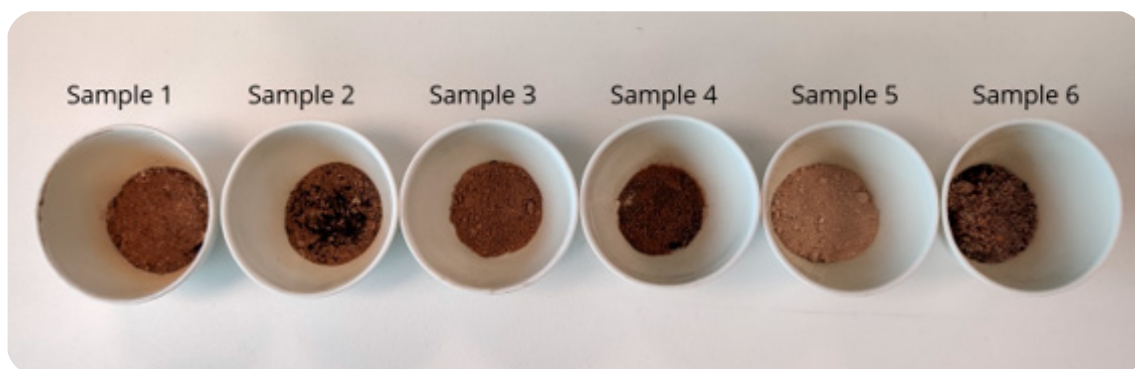
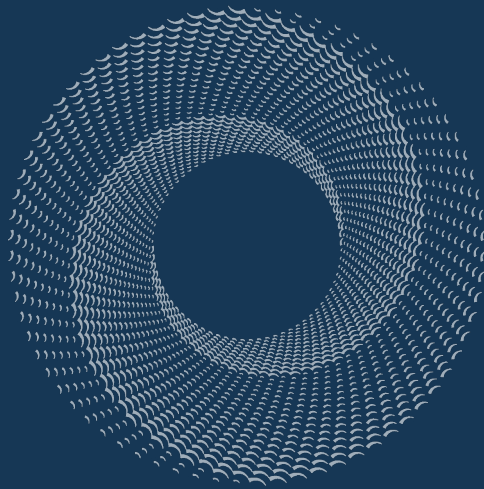


Fig. 7 Char products collected from pyrolysis of Samples 1–6.  
The char residues showed differences in colour, texture and amount between the samples.

The oil/wax products showed visible differences in colour and physical appearance, ranging from lighter liquid-like fractions to darker and more wax-like products. The char products also differed in colour, texture and amount, which reflects differences in material composition, contamination level and inorganic residue content between the samples.

# 5. Density of oil/wax products





# 5. Density of oil/wax products

The density of the oil/wax products was determined for Samples 1–6. The density was calculated by weighing a 10 mL measuring glass before and after addition of 10 mL oil/wax product. The mass of the oil/wax product was then divided by the measured volume to obtain the density in g/mL.

For Sample 1, both a light fraction and a heavy fraction were measured. However, in the main report, only the average density of Sample 1 is presented in order to allow direct comparison with the other samples. The detailed density results, including the light and heavy fractions for Sample 1, are included in Appendix B.

The measured densities of the oil/wax products are shown in Table 3.

Table 3 Density of oil/wax products.

| Sample   | Fraction | Density (g/mL) |
|----------|----------|----------------|
| Sample 1 | Oil/wax  | 0.79           |
| Sample 2 | Oil/wax  | 0.80           |
| Sample 3 | Oil/wax  | 0.76           |
| Sample 4 | Oil/wax  | 0.81           |
| Sample 5 | Oil/wax  | 0.71           |
| Sample 6 | Oil/wax  | 0.81           |

The measured densities were in the range of 0.708–0.811 g/mL. Sample 5, the contaminated Aarhus River PE sample, had the lowest density, while Sample 4, the washed Aarhus River PP sample, had the highest density. Sample 6, virgin PE, also showed a relatively high density, close to Sample 4 and Sample 2.

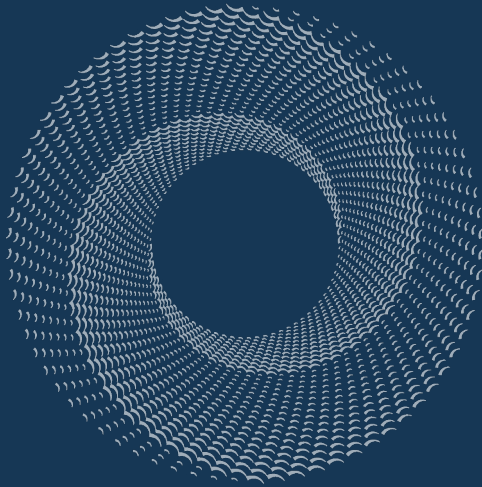
For the PP samples, Samples 1–4, the densities were relatively close, ranging from 0.764 to 0.811 g/mL. This indicates that the PP-derived oil/wax products had broadly similar densities, although some variation was observed between contaminated, washed, and virgin PP samples. Sample 1 had an average density of 0.786 g/mL, based on the light and heavy fractions measured separately.

For the PE samples, Samples 5 and 6, a larger difference was observed. Sample 5 had the lowest density of all samples, while Sample 6 showed a density similar to the higher-density PP oil/wax products. This indicates that the composition of the PE-derived oil/wax products differed between the contaminated Aarhus River PE and the virgin PE reference sample.

Overall, the density results show that the oil/wax products from the pyrolysis experiments were in a comparable density range, but with measurable differences between sample types. These differences may be related to variations in the relative amount of light and heavy hydrocarbon compounds, wax content, and material composition.



**6.**  
**Total acid number (TAN)**  
**of oil/wax products**





## 6. Total acid number (TAN) of oil/wax products

The total acid number (TAN) was determined for the oil/wax products from Samples 1–6. The TAN value expresses the amount of potassium hydroxide (KOH) required to neutralise acidic compounds in one gram of oil/wax product and is reported as mg KOH/g oil. A higher TAN value indicates a higher content of acidic compounds in the pyrolysis oil/wax product.

Each sample was analysed twice, and the average TAN value was calculated from the two measurements. The detection limit was below 0.2 mg KOH/g oil. The results are shown in Table 4.

Table 4 Total acid number of oil/wax products.

| Sample   | TAN, test 1(mg KOH/g oil) | TAN, test 2 (mg KOH/g oil) | Average TAN (mg KOH/g oil) |
|----------|---------------------------|----------------------------|----------------------------|
| Sample 1 | 4.1                       | 4.4                        | 4.2                        |
| Sample 2 | 1.4                       | 1.2                        | 1.3                        |
| Sample 3 | 0.6                       | 0.5                        | 0.5                        |
| Sample 4 | 0.5                       | 0.4                        | 0.4                        |
| Sample 5 | 0.4                       | 0.4                        | 0.4                        |
| Sample 6 | .02                       | 0.3                        | 0.2                        |

The TAN results show that Sample 1 had the highest acid number, with an average value of 4.2 mg KOH/g oil.

Sample 2, which was also contaminated Aarhus River PP, had a lower average TAN value of 1.3 mg KOH/g oil. The virgin PP reference, Sample 3, had an average TAN value of 0.5 mg KOH/g oil, while the washed Aarhus River PP sample, Sample 4, had a slightly lower value of 0.4 mg KOH/g oil.

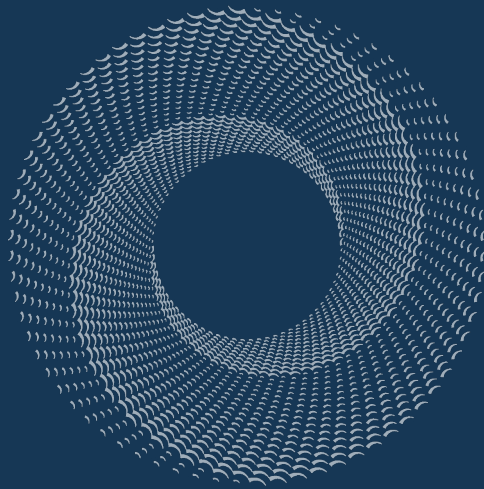
For the PP samples, the results indicate that the contaminated Aarhus River PP samples generally produced oil/wax products with higher TAN values than the virgin and washed PP samples. This suggests that contamination, degradation products, or oxygen-containing compounds associated with the river-collected material may have contributed to the acidity of the pyrolysis oil/wax products. The lower TAN value for Sample 4 indicates that washing may have reduced part of the acidic or contamination-related contribution, although the value was still above the detection limit.

For the PE samples, Samples 5 and 6, the TAN values were lower than for most PP samples. Sample 5, contaminated Aarhus River PE, had an average TAN value of 0.4 mg KOH/g oil, while Sample 6, virgin PE, had the lowest average TAN value of 0.2 mg KOH/g oil. This indicates that the PE-derived oil/wax products contained relatively low amounts of acidic compounds. The slightly higher TAN value for Sample 5 compared with Sample 6 may be related to contamination or degradation products present in the river-collected PE fraction.

Overall, the TAN results show that the acidity of the pyrolysis oil/wax products varied between the samples. The highest TAN values were observed for contaminated Aarhus River PP, especially Sample 1, while the lowest value was observed for virgin PE. The results suggest that contamination and sample condition can influence the acidity of the oil/wax products. In general, the cleaner reference materials and the washed PP sample showed lower TAN values than the contaminated PP samples.

# 7.

## FTIR Analysis of pyrolysis samples



## 7. FTIR Analysis of pyrolysis samples

### 7.1 Purpose of FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) was used as a qualitative analytical method to investigate the main chemical structures and functional groups present in the pyrolysis products. The analysis was performed on both the oil/wax products and the solid residue/char products from the PP- and PE pyrolysis samples.

The purpose of the FTIR analysis of the oil/wax products was to evaluate whether the liquid/waxy fractions were mainly composed of hydrocarbon structures originating from the thermal cracking of polypropylene and polyethylene. The analysis focused on identifying characteristic absorption bands related to aliphatic C–H stretching, CH<sub>2</sub> and CH<sub>3</sub> bending vibrations, unsaturated hydrocarbon structures, and long-chain hydrocarbon structures. This made it possible to compare the products obtained from contaminated Aarhus River plastic, washed Aarhus River plastic, and virgin reference materials.

The purpose of the FTIR analysis of the char products was to evaluate the chemical nature of the solid residues remaining after pyrolysis. The char fractions were analysed to determine whether they still contained residual organic or carbonaceous material and whether inorganic or mineral-related structures were present. In addition, selected char samples were analysed after ashing in order to better evaluate the inorganic/mineral residue after removal of remaining organic material.

FTIR library matching was used as a supporting tool for qualitative interpretation. However, the library matches should not be interpreted as exact compound identification, especially for the oil/wax products and char residues, because these samples are complex mixtures. Therefore, the FTIR results were mainly used to identify functional groups and compare overall spectral profiles between samples. More detailed identification of individual organic compounds in the oil/wax products should be based on GC-MS analysis.

### 7.2 FTIR analysis of oil/wax and char products

#### 7.2.1 Sample 1

##### FTIR analysis of Sample 1 oil/wax

The FTIR results for Sample 1 show that both the light and heavy oil/wax fractions were mainly composed of aliphatic hydrocarbons with clear indications of alkene structures. The repeated measurements showed very similar peak patterns and library matches, confirming good repeatability. The results



are consistent with the expected formation of saturated and unsaturated hydrocarbon compounds during thermal cracking of polypropylene. The FTIR library matches should be interpreted as qualitative indications only, because FTIR cannot provide exact compound identification in complex pyrolysis oil/wax mixtures. More detailed identification of individual compounds should therefore be based on GC-MS analysis.

### **FTIR analysis of Sample 1 char**

The FTIR results for Sample 1 char show that the solid residue differs clearly from the oil/wax products. While the oil/wax fractions were mainly dominated by aliphatic and unsaturated hydrocarbons from PP degradation, the char showed weaker hydrocarbon bands and stronger contributions from oxygen-containing and inorganic/mineral-related structures. This supports that contamination and inorganic residues from the river-collected material were concentrated in the solid char fraction after pyrolysis.

## **7.2.2 Sample 2**

### **FTIR analysis of Sample 2 oil/wax**

The repeated FTIR measurements showed almost identical peak patterns and very similar library match results. This indicates good repeatability of the FTIR analysis for Sample 2. The results are also highly comparable with the oil/wax results obtained for Sample 1, supporting that both contaminated Aarhus River PP pyrolysis tests produced oil/wax products dominated by aliphatic and unsaturated hydrocarbons. This is consistent with the expected thermal cracking of polypropylene during pyrolysis.

As for Sample 1, the FTIR library matches should be interpreted as qualitative indications only. The oil/wax product is a complex mixture of pyrolysis compounds, and FTIR cannot provide exact identification of individual compounds. More detailed compound identification should therefore be based on GC-MS analysis.

### **FTIR analysis of Sample 2 char**

The FTIR results for Sample 2 char show that the solid residue is not dominated by polypropylene-like hydrocarbon structures. Instead, it contains a mixture of residual carbonaceous material, oxygen-containing groups, and inorganic/mineral residues. This differs clearly from the Sample 2 oil/wax product, which was dominated by aliphatic and unsaturated PP-derived hydrocarbons. The results support that inorganic contamination from the river-collected material was concentrated in the char fraction after pyrolysis.

### 7.2.3 Sample 3

#### FTIR analysis of Sample 3 oil/wax

The FTIR results for Sample 3 show that pyrolysis of virgin PP produced an oil/wax product dominated by aliphatic hydrocarbons and alkene structures. The results are consistent with the expected degradation products from polypropylene. As with the other oil/wax samples, the FTIR library matches should be interpreted as qualitative indications only, since FTIR cannot identify individual compounds in complex pyrolysis mixtures. More detailed compound identification should therefore be based on GC-MS analysis.

#### FTIR analysis of Sample 3 char

The FTIR results for Sample 3 char show that the solid residue is not dominated by polypropylene-like hydrocarbon structures. The char contains small amounts of residual hydrocarbon or carbonaceous material, but the main spectral features are associated with oxygen-containing and inorganic/mineral-related residues. Compared with the char from the contaminated Aarhus River PP samples, Sample 3 is expected to represent a cleaner reference char. However, the presence of inorganic/mineral-related bands indicates that even virgin PP pyrolysis can leave an inorganic ash residue, possibly originating from additives, fillers, sample preparation, or small residual inorganic components.

### 7.2.4 Sample 4

#### FTIR analysis of Sample 4 oil/wax

The FTIR results for Sample 4 show that pyrolysis of washed Aarhus River PP produced an oil/wax product dominated by aliphatic hydrocarbons and alkene structures. The results are consistent with the expected degradation products from polypropylene and are comparable with the oil/wax products from both contaminated Aarhus River PP and virgin PP. As with the other oil/wax samples, the FTIR library matches should be interpreted as qualitative indications only, and detailed compound identification should be based on GC-MS analysis.

#### FTIR analysis of Sample 4 char

The FTIR results for Sample 4 char indicate that washing reduced visible contamination but did not remove all inorganic or mineral-related residues. The char from washed Aarhus River PP was not dominated by polypropylene-like hydrocarbon structures. Instead, it contained residual carbonaceous material together with oxygen-containing and inorganic/mineral-related structures. Compared with the dirty PP char samples, Sample 4 is expected to contain fewer external contaminants, but the FTIR and XRF results indicate that some inorganic residues remained in the char fraction after pyrolysis.

## 7.2.5 Comparison of PP products - Samples 1–4

### Comparison of PP Oil/wax FTIR spectra

The FTIR spectra of the oil/wax products from Samples 1–4 are shown together in Figure 8.

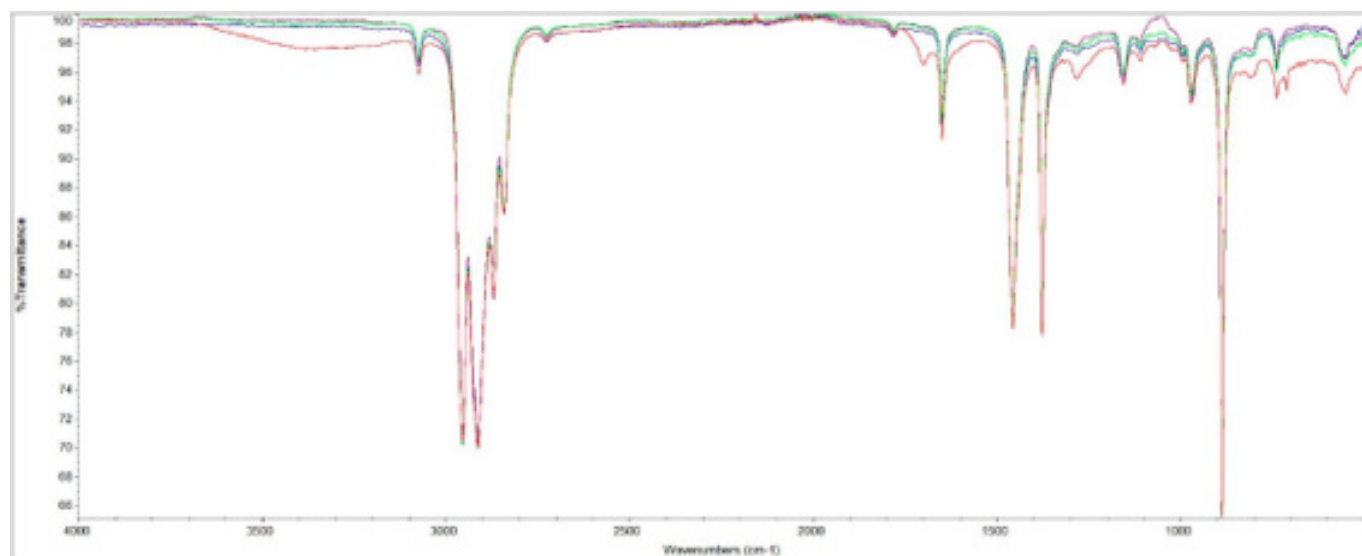


Fig. 8 Combined FTIR spectra of oil/wax products from PP pyrolysis samples. Sample 1: contaminated Aarhus River PP (red), Sample 2: contaminated Aarhus River PP repeat (purple), Sample 3: virgin PP (green), and Sample 4: washed Aarhus River PP (blue).

The FTIR spectra of the oil/wax products from Samples 1–4 are compared in Figure 8. Sample 1 and Sample 2 represent contaminated Aarhus River PP, Sample 3 represents virgin PP, and Sample 4 represents washed Aarhus River PP.

All four spectra showed very similar peak patterns, indicating that the oil/wax products from the PP samples had comparable chemical structures. Overall, the combined FTIR comparison indicates that all PP oil/wax products were mainly composed of aliphatic and unsaturated hydrocarbons formed during thermal cracking of polypropylene. The results suggest that contamination from the river-collected PP was mainly concentrated in the solid char/ash fraction rather than in the oil/wax product. More detailed identification of individual compounds should be based on GC-MS analysis.





## Comparison of PP char FTIR spectra

The FTIR spectra of the char fractions from Samples 1–4 are compared in Figure 9.

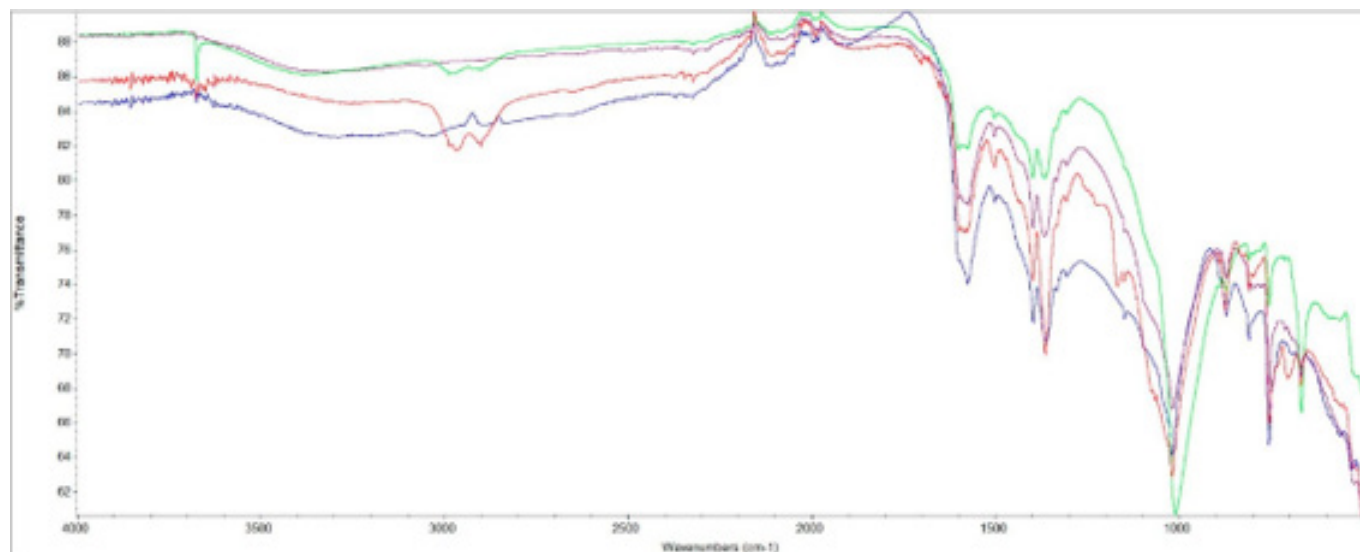


Fig. 9 Combined FTIR spectra of char fractions from PP pyrolysis samples. Sample 1: contaminated Aarhus River PP (red), Sample 2: contaminated Aarhus River PP repeat (purple), Sample 3: virgin PP (green), and Sample 4: washed Aarhus River PP (blue).

The FTIR spectra of the char fractions from Samples 1–4 are compared in Figure 9. Sample 1 and Sample 2 represent contaminated Aarhus River PP, Sample 3 represents virgin PP, and Sample 4 represents washed Aarhus River PP.

Compared with the corresponding oil/wax spectra, the char spectra showed broader and less uniform absorption patterns. Overall, the combined char FTIR comparison indicates that the PP char fractions were chemically more complex than the oil/wax products. While the oil/wax spectra from Samples 1–4 were very similar and dominated by PP-derived hydrocarbons, the char spectra showed stronger differences and broader bands related to carbonaceous and inorganic/mineral residues. This supports the interpretation that contamination and inorganic residues from the river-collected PP were mainly concentrated in the solid char/ash fraction rather than in the oil/wax product.

## Comparison of PP ashed char FTIR spectra

The FTIR spectra of the ashed char fractions from Samples 1–4 are compared in Figure 10.



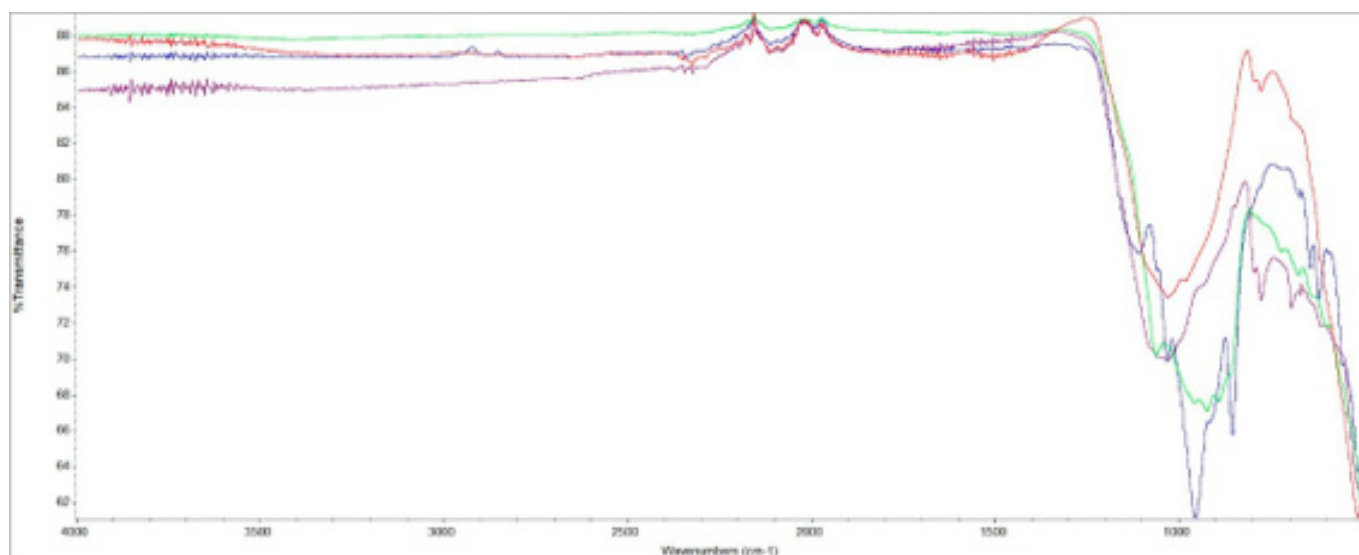


Fig. 10 Combined FTIR spectra of ashed char fractions from PP pyrolysis samples. Sample 1: contaminated Aarhus River PP (red), Sample 2: contaminated Aarhus River PP repeat (purple), Sample 3: virgin PP (green), and Sample 4: washed Aarhus River PP (blue).

The FTIR spectra of the ashed char fractions from Samples 1–4 are compared in Figure 10. Sample 1 and Sample 2 represent contaminated Aarhus River PP, Sample 3 represents virgin PP, and Sample 4 represents washed Aarhus River PP.

Compared with the non-ashed char spectra, the ashed char spectra showed a reduction in hydrocarbon-related bands. Overall, the combined FTIR comparison of the ashed char fractions indicates that the remaining residues after ashing were mainly inorganic/mineral-like rather than PP-derived organic material. Compared with the oil/wax products, which showed very similar PP-derived hydrocarbon profiles, the ashed char fractions showed stronger differences between samples. This supports the interpretation that inorganic contamination and ash-forming components were mainly concentrated in the char/ash fraction rather than transferred into the oil/wax product.

## 7.2.6 Sample 5

### FTIR analysis of Sample 5 oil/wax

The oil/wax product from Sample 5, contaminated polyethylene collected from Aarhus River, was analysed by FTIR. Sample 5 represented the dirty/untreated PE fraction and consisted of approximately 60% LDPE and 40% HDPE.

Overall, the FTIR results for Sample 5 indicate that pyrolysis of contaminated Aarhus River PE produced an oil/wax product dominated by long-chain aliphatic hydrocarbons. The high library match values to polyethylene-related materials and long-chain hydrocarbons support that the oil/wax product is mainly derived from PE degradation. As with the other oil/wax samples, the FTIR results should be interpreted qualitatively, and more detailed compound identification should be based on GC-MS

analysis.

### **FTIR analysis of Sample 5 char**

The solid residue/char obtained from pyrolysis of Sample 5, contaminated polyethylene collected from Aarhus River, was analysed by FTIR. Sample 5 represented the dirty/untreated PE fraction and consisted of approximately 60% LDPE and 40% HDPE. Compared with the oil/wax product from Sample 5, the char showed a clearly different FTIR profile.

Overall, the FTIR results for Sample 5 char indicate that the solid residue from contaminated Aarhus River PE is not dominated by polyethylene-like hydrocarbon structures. Instead, it contains residual carbonaceous material together with additive-, filler-, and inorganic/mineral-related components. This differs clearly from the Sample 5 oil/wax product, which was dominated by long-chain aliphatic hydrocarbons. The results suggest that inorganic contamination, fillers, pigments, additives, or other non-polymeric residues from the river-collected PE were concentrated in the char fraction after pyrolysis.

## **7.2.7 Sample 6**

### **FTIR analysis of Sample 6 oil/wax**

The oil/wax product from Sample 6, virgin polyethylene, was analysed by FTIR. Sample 6 was included as a clean PE reference material for comparison with the oil/wax product obtained from contaminated Aarhus River PE in Sample 5.

Overall, the FTIR results for Sample 6 indicate that pyrolysis of virgin PE produced an oil/wax product mainly composed of long-chain aliphatic hydrocarbons and wax-like compounds. The high library match values to polyethylene-related materials and long-chain hydrocarbons are consistent with the expected degradation products from polyethylene. As with the other oil/wax samples, the FTIR library matches should be interpreted as qualitative indications only, and detailed compound identification should be based on GC-MS analysis.

### **FTIR analysis of Sample 6 char**

The solid residue/char obtained from pyrolysis of Sample 6, virgin polyethylene, was analysed by FTIR. Sample 6 was included as a clean PE reference material for comparison with the char obtained from contaminated Aarhus River PE in Sample 5.

Compared with the oil/wax product from Sample 6, the char showed a clearly different FTIR profile. Overall, the FTIR results for Sample 6 char indicate that the solid residue from virgin PE pyrolysis

was not dominated by polyethylene-like hydrocarbon structures. Instead, the char contained small amounts of residual carbonaceous material together with oxygen-containing and inorganic/mineral-related structures. Compared with Sample 5, the contaminated Aarhus River PE char, Sample 6 is expected to represent a cleaner PE reference char. However, the presence of inorganic/mineral-related bands shows that even virgin PE can leave an ash residue after pyrolysis, possibly originating from additives, fillers, pigments, processing residues, or sample preparation.

## 7.2.8 Comparison of PE products - Samples 5-6

### Comparison of PE oil/wax FTIR spectra

The FTIR spectra of the oil/wax products from Samples 5 and 6 are compared in Figure 11.

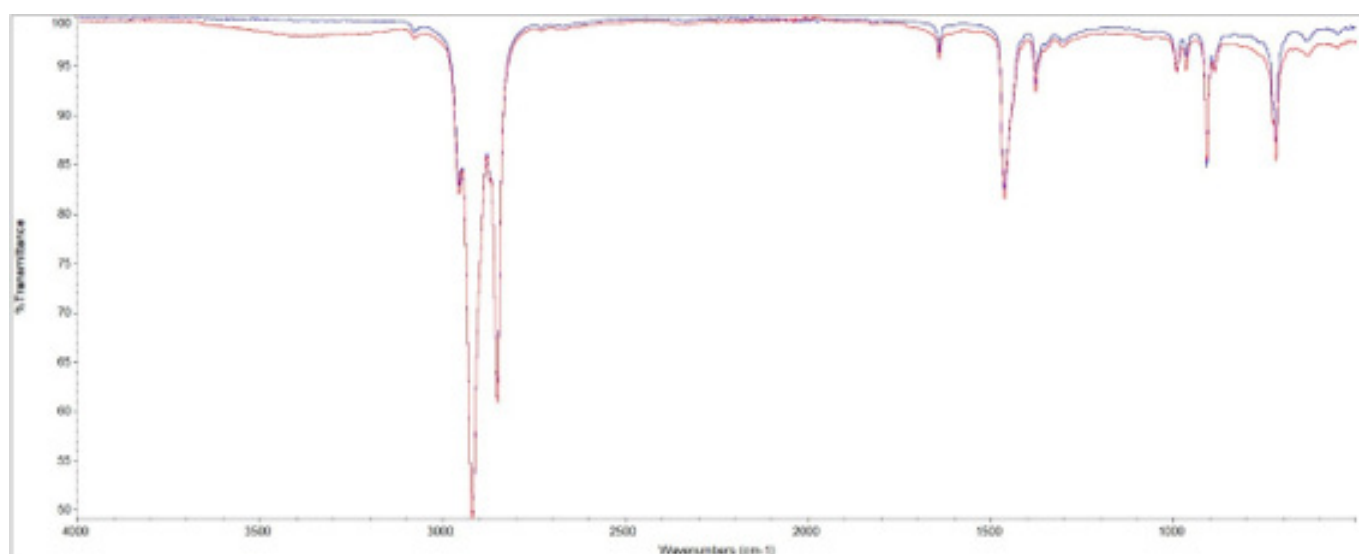


Fig. 11 Combined FTIR spectra of oil/wax products from PE pyrolysis samples. Sample 5: contaminated Aarhus River PE (red), and Sample 6: virgin PE (blue).

The FTIR spectra of the oil/wax products from Samples 5 and 6 showed very similar peak patterns. Sample 5 represents contaminated Aarhus River PE, while Sample 6 represents virgin PE used as a clean reference material. The close overlap between the two spectra indicates that both PE samples produced oil/wax products with comparable chemical structures.

Overall, the combined FTIR comparison indicates that both PE oil/wax products were mainly composed of long-chain aliphatic hydrocarbons formed during thermal cracking of polyethylene. The results suggest that contamination from the river-collected PE did not significantly change the main FTIR profile of the oil/wax product. More detailed identification of individual compounds should be based on GC-MS analysis.

### Comparison of PE char FTIR spectra

The FTIR spectra of the char fractions from Samples 5 and 6 are compared in Figure 12.

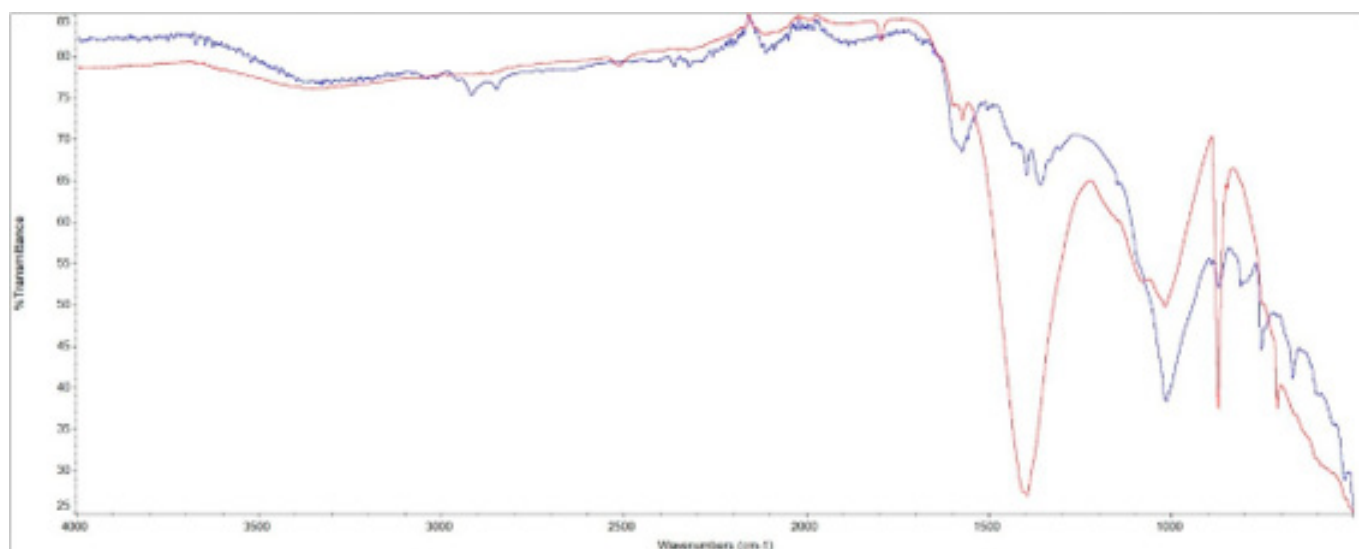


Fig. 12 Combined FTIR spectra of char fractions from PE pyrolysis samples. Sample 5: contaminated Aarhus River PE (red), and Sample 6: virgin PE (blue).

The FTIR spectra of the char fractions from Samples 5 and 6 showed broader and less uniform absorption patterns compared with the corresponding oil/wax spectra. Sample 5 represents contaminated Aarhus River PE, while Sample 6 represents virgin PE used as a clean reference material.

Overall, the combined FTIR comparison shows that the PE char fractions were chemically more complex than the PE oil/wax products. While the oil/wax spectra from Samples 5 and 6 were very similar and dominated by PE-derived long-chain hydrocarbons, the char spectra showed stronger differences and broader bands related to carbonaceous and inorganic/mineral residues. This supports the interpretation that contamination, additives, fillers, pigments, and inorganic residues were mainly concentrated in the solid char/ash fraction rather than transferred into the oil/wax product.

### Comparison of PE ashed char FTIR spectra

The FTIR spectra of the ashed char fractions from Samples 5 and 6 are compared in Figure 13.



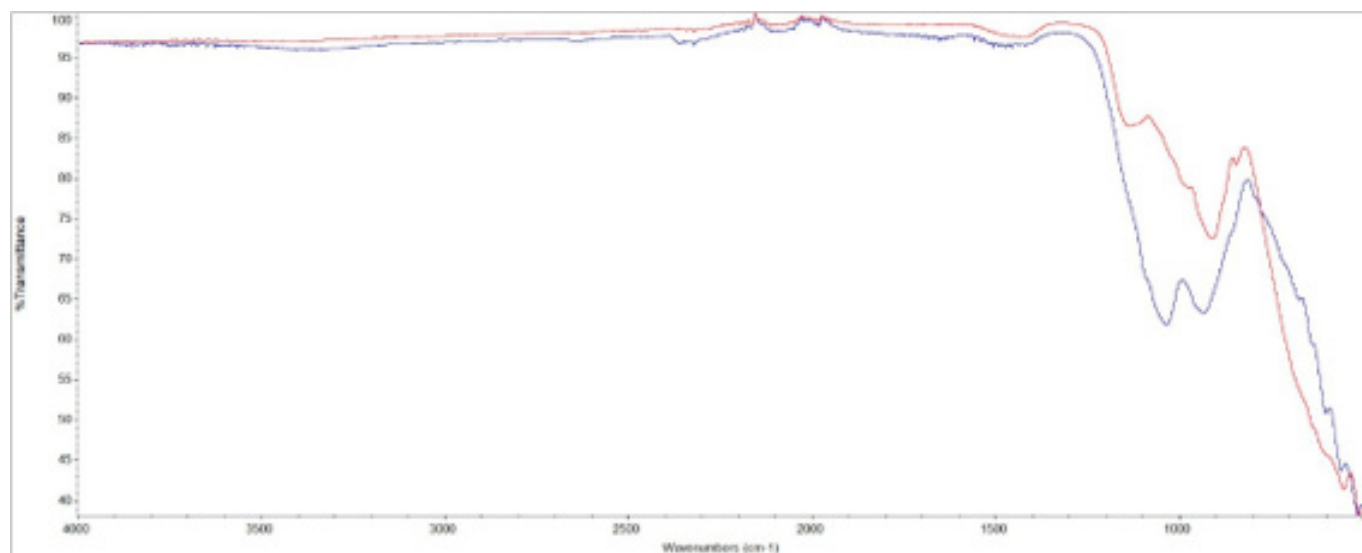


Fig. 13 Combined FTIR spectra of ashed char fractions from PE pyrolysis samples.  
Sample 5: contaminated Aarhus River PE (red), and Sample 6: virgin PE (blue).

The FTIR spectra of the ashed char fractions from Samples 5 and 6 showed a clear reduction in hydrocarbon-related bands compared with the non-ashed char spectra.

Overall, the combined FTIR comparison of the PE ashed char fractions indicates that inorganic and ash-forming components were concentrated in the char/ash fraction after pyrolysis. The results support the interpretation that the main PE-derived hydrocarbons were transferred to the oil/wax product, while inorganic residues, fillers, pigments, additives, and contamination remained in the solid residue.

### 7.3 Comparison and interpretation

The FTIR results showed clear differences between the oil/wax products and the char fractions obtained from pyrolysis. The oil/wax products from the PP samples were dominated by absorption bands characteristic of aliphatic and unsaturated hydrocarbons.

The oil/wax products from the PE samples showed a different but clearly hydrocarbon-dominated profile. These bands are typical for long-chain polyethylene-like or paraffinic hydrocarbon structures. This indicates that pyrolysis of PE produced oil/wax products mainly composed of long-chain aliphatic hydrocarbons and wax-like compounds.

The comparison between contaminated, washed, and virgin samples showed that the oil/wax products from the same polymer type were highly similar. For the PP samples, the spectra of contaminated Aarhus River PP, washed Aarhus River PP, and virgin PP showed close overlap and similar peak patterns. This indicates that the main oil/wax products from these samples were chemically similar

and mainly derived from PP degradation. Washing did not significantly change the main FTIR profile of the PP oil/wax product. Similarly, the oil/wax spectra of contaminated Aarhus River PE and virgin PE were very similar, indicating that the contaminated PE sample also produced an oil/wax fraction dominated by PE-derived hydrocarbons.

In contrast, the char fractions showed broader and more complex FTIR profiles than the oil/wax products. The hydrocarbon-related C-H stretching bands were much weaker in the char spectra, indicating that only smaller amounts of residual organic or carbonaceous material remained in the solid residue after pyrolysis. These bands may be associated with C-O stretching vibrations, Si-O-related structures, silicate-type residues, metal oxides, fillers, pigments, additives, or other inorganic/mineral-related components.

The ashed char spectra supported this interpretation. After ashing, the hydrocarbon-related bands were strongly reduced or almost absent, while broad absorption features in the lower wavenumber region became dominant. This indicates that the remaining material after ashing was mainly inorganic or mineral-like rather than polymer-derived organic material. The FTIR results are therefore consistent with the XRF results, which showed measurable inorganic elements in the char samples.

Overall, the FTIR results indicate that pyrolysis transferred the main polymer-derived hydrocarbons into the oil/wax fraction, while inorganic contamination, fillers, pigments, additives, and ash-forming components were mainly concentrated in the char/ash fraction.

This was observed for both PP and PE samples. The results also show that contamination from the river-collected plastic did not strongly change the main chemical profile of the oil/wax products, but it had a stronger influence on the composition of the solid residue.

## 7.4 Summary FTIR

FTIR analysis was used to evaluate the main chemical structures present in the oil/wax and char products from pyrolysis of PP and PE samples. The results showed that the oil/wax products were mainly composed of hydrocarbon structures derived from the original polymer materials.

The PP oil/wax products from Samples 1–4 showed very similar FTIR spectra. This indicates that contaminated Aarhus River PP, washed Aarhus River PP, and virgin PP all produced oil/wax products dominated by PP-derived aliphatic and alkene-type hydrocarbons. The PE oil/wax products from Samples 5 and 6 also showed very similar spectra. These spectra were dominated by strong CH<sub>2</sub> stretching, CH<sub>2</sub> bending, and CH<sub>2</sub> rocking vibrations, which are characteristic of long-chain

polyethylene-like or paraffinic hydrocarbons. This supports the conclusion that both contaminated Aarhus River PE and virgin PE produced oil/wax products mainly composed of long-chain aliphatic hydrocarbons.

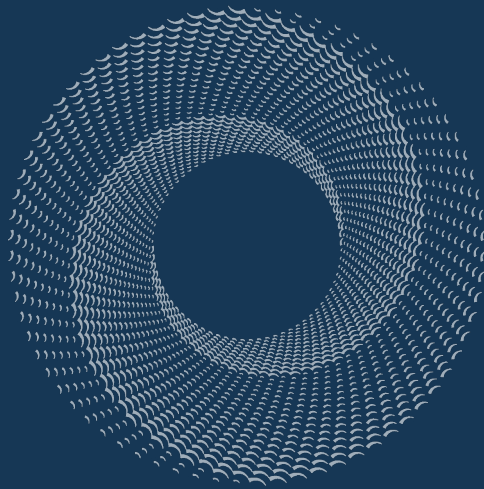
The char products showed different FTIR profiles compared with the oil/wax products. The hydrocarbon-related bands were weaker, while broader absorption features were observed in the fingerprint region, especially around 1100–900 cm<sup>-1</sup>. These features indicate the presence of residual carbonaceous material together with oxygen-containing and inorganic/mineral-related structures.

The ashed char samples showed further reduction of organic hydrocarbon bands and stronger mineral-related absorption features. This indicates that the remaining residues after ashing were mainly inorganic or mineral-like. The FTIR results therefore support the XRF results, which showed that inorganic elements were retained in the char fraction.

Overall, the FTIR analysis shows that the main oil/wax products from pyrolysis were dominated by polymer-derived hydrocarbons, while contamination, additives, fillers, pigments, and inorganic residues were mainly concentrated in the char/ash fraction. The FTIR results should be considered qualitative, and detailed identification of individual compounds in the oil/wax products should be based on GC-MS analysis.

# 8.

## GC-MS Analysis of oil/wax products



## 8. GC-MS Analysis of oil/wax products

### 8.1 Purpose of GC-MS analysis

Gas Chromatography coupled with Mass Spectrometry (GC-MS) was used to analyse the organic composition of the oil/wax products obtained from pyrolysis of the PP and PE samples. The purpose of the GC-MS analysis was to identify the main types of organic compounds present in the oil/wax products and to compare the products obtained from contaminated Aarhus River plastic, washed Aarhus River plastic and virgin reference materials.

The GC-MS analysis separates compounds according to their retention time and provides mass spectral information that can be used to suggest possible compound identities. In this study, the focus was mainly on identifying compound groups, such as alkanes, alkenes, cyclic hydrocarbons, alcohols and possible ester-type compounds. The results should be interpreted qualitatively. The oil/wax products are complex pyrolysis mixtures, and some compounds may overlap or co-elute in the chromatograms. In particular, it can be difficult to distinguish between fragmentation patterns from alkanes and alcohols. Therefore, the identified compounds should be considered possible or likely components rather than exact compound identifications.

The oil/wax samples were dissolved in dichloromethane,  $\text{CH}_2\text{Cl}_2$ , at approximately 10% concentration before analysis. The GC-MS analysis was performed using a temperature programme from 60 °C to 275 °C.

A summary of the main compound groups identified by GC-MS is shown in Table 5. The full component identification tables and chromatograms are included in Appendix E.

Table 5 Summary of main compound groups identified by GC-MS.

| Samples    | Polymer type | Main compound groups identified                                                            |
|------------|--------------|--------------------------------------------------------------------------------------------|
| Sample 1–4 | PP oil/wax   | Alkanes, alkenes, cyclic hydrocarbons, possible alcohols and possible ester-type compounds |
| Sample 5–6 | PE oil/wax   | Mainly unbranched alkanes and alkenes from approximately C10 to >C26                       |



## 8.2 GC-MS analysis of PP oil/wax products

The GC-MS results for Samples 1–4 showed that the PP oil/wax products contained a complex mixture of hydrocarbons.

Overall, the GC-MS results indicate that the PP oil/wax products were mainly composed of hydrocarbons, especially alkanes, alkenes and cyclic hydrocarbon structures. This is consistent with the FTIR results, where the PP oil/wax products showed strong aliphatic C–H bands and bands related to unsaturated hydrocarbons. The presence of branched and cyclic hydrocarbons is also consistent with the expected thermal degradation of polypropylene, since PP has a branched polymer structure.

## 8.3 GC-MS analysis of PE oil/wax products

The GC-MS results for Samples 5 and 6 showed a clear homologous series of hydrocarbon compounds. The results are consistent with the expected pyrolysis products from polyethylene. PE pyrolysis typically produces long-chain linear hydrocarbons, including alkanes and alkenes. The presence of a regular series of C<sub>10</sub> to >C<sub>26</sub> hydrocarbons indicates that the PE oil/wax products were dominated by long-chain aliphatic compounds. These results are also consistent with the FTIR analysis. These FTIR bands are characteristic of long-chain polyethylene-like or paraffinic hydrocarbon structures, which supports the GC-MS interpretation.

## 8.4 Comparison and interpretation

The GC-MS results show clear differences between the PP- and PE-derived oil/wax products.

The PP oil/wax products from Samples 1–4 contained a more complex mixture of branched, cyclic and unsaturated hydrocarbons. Possible components included branched alkanes and alkenes, cyclic alkanes, cyclic alkenes and longer-chain hydrocarbons. Some possible alcohols and ester-type compounds were also suggested, but these identifications should be interpreted with caution because the fragmentation patterns of alkanes and alcohols can be difficult to distinguish.

The PE oil/wax products from Samples 5 and 6 showed a more regular hydrocarbon pattern. The main components were identified as unbranched alkanes and alkenes from approximately C<sub>10</sub> to above C<sub>26</sub>.

This indicates that PE pyrolysis produced a more linear series of long-chain hydrocarbons compared with the PP samples.

This difference is consistent with the chemical structure of the original polymers. Polypropylene has

a methyl side group on the polymer chain, which can lead to more branched and cyclic degradation products during pyrolysis. Polyethylene has a simpler linear hydrocarbon backbone, which is more likely to form long-chain linear alkanes and alkenes during thermal cracking.

The GC-MS results also support the FTIR interpretation. FTIR showed that all oil/wax products were dominated by hydrocarbon structures, while GC-MS provided more detailed information about the type of hydrocarbons present. The PP oil/wax products were mainly associated with aliphatic, unsaturated, branched and cyclic hydrocarbons, while the PE oil/wax products were dominated by long-chain alkanes and alkenes.

The comparison between contaminated and virgin samples indicates that the main oil/wax products were primarily determined by polymer type. For both PP and PE, the main GC-MS results were consistent with polymer-derived hydrocarbon products. This supports the interpretation that contamination from the river-collected material was mainly retained in the char/ash fraction, while the oil/wax fraction mainly consisted of pyrolysis hydrocarbons from the plastic polymers.

## 8.5 Summary GC-MS

GC-MS analysis was used to evaluate the organic composition of the oil/wax products from pyrolysis of PP- and PE samples. The analysis showed that all oil/wax products were mainly composed of hydrocarbon compounds.

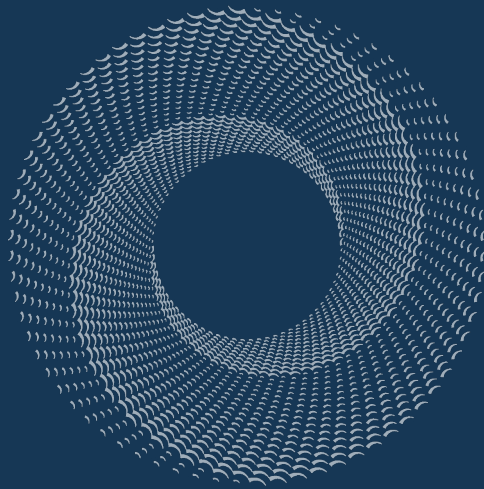
The PP oil/wax products from Samples 1–4 contained a complex mixture of alkanes, alkenes and cyclic hydrocarbon structures. Possible alcohols and ester-type compounds were also indicated in some retention time regions, but these assignments should be interpreted cautiously due to possible overlap and similarity in fragmentation patterns.

The PE oil/wax products from Samples 5 and 6 showed a clearer homologous series of mainly unbranched alkanes and alkenes from approximately C10 to above C26. This indicates that PE pyrolysis produced oil/wax products dominated by long-chain aliphatic hydrocarbons.

Overall, the GC-MS results support the FTIR results. The oil/wax products were mainly composed of polymer-derived hydrocarbons, while contamination, inorganic residues, fillers, pigments and additives were more strongly associated with the char/ash fraction, as shown by FTIR, XRF and TGA. The GC-MS results also show that polymer type had a strong influence on the oil/wax composition, with PP producing more branched and cyclic hydrocarbon structures and PE producing more linear long-chain hydrocarbons.

# 9.

## XRF analysis of solid residue/char



# 9. XRF analysis of solid residue/char

## 9.1 Purpose of XRF analysis

X-Ray Fluorescence (XRF) analysis was used to determine the inorganic elemental composition of the solid residue/char products after pyrolysis. The purpose of the analysis was to evaluate whether the char samples contained inorganic residues originating from contamination, mineral particles, pigments, fillers, soil, or other non-polymeric material present in the plastic fractions.

Since PP and PE are organic polymers mainly consisting of carbon and hydrogen, the presence of inorganic elements such as Si, Ca, Fe, Al, Cl, Ti, Pb, Cu, Zn, Mg, S, and P indicates that inorganic material was retained in the char fraction after pyrolysis. This inorganic material may originate from external contamination, additives, fillers, pigments, labels, or mineral particles attached to the plastic surface. The XRF results are reported as percentages. The results should be interpreted as semi-quantitative, as the char samples are heterogeneous and the measured composition may depend on the specific particles analysed. The full XRF results for all samples and the graphs with the percentages are presented in Appendix D. A summary of the dominant inorganic elements is shown in Table 6.

Table 6 Summary of dominant inorganic elements in char samples determined by XRF.

| Sample   | Light elements (%) | Dominant inorganic elements (%)                        |
|----------|--------------------|--------------------------------------------------------|
| Sample 1 | 63.6%              | Si 8.1%, Ca 7.9%, Fe 5.7%, Al 3.0%, Pb 2.7%, Cl 2.1%   |
| Sample 2 | 33.3%              | Cu 16.5%, Fe 10.7%, Si 9.1%, Ca 8.0%, Pb 6.7%, Al 5.5% |
| Sample 3 | 52.0%              | Si 11.3%, Fe 8.1%, Ca 8.1%, Mg 5.5%, Al 4.9%, Cl 2.9%  |
| Sample 4 | 65.6%              | Ca 10.7%, Cl 7.8%, Si 5.8%, Fe 2.6%, Al 2.5%, Mg 2.0%  |
| Sample 5 | 59.3%              | Ca 18.2%, Ti 12.3%, Si 3.5%, Cl 2.0%, Al 1.6%, Fe 1.4% |
| Sample 6 | 79.4%              | Si 5.0%, Ca 4.3%, Fe 3.8%, Cl 2.1%, Al 2.0%, Ti 1.4%   |

As shown in Table 6, all char samples contained a high fraction of light elements together with measurable amounts of inorganic elements. The most frequently detected dominant elements were Si, Ca, Fe, Al, Cl, Mg, Ti, Cu, Pb, and Zn. This indicates that inorganic residues remained in the solid char fraction after pyrolysis.

## 9.2 XRF analysis of PP char products

The XRF analysis of the PP char samples showed that the solid residue contained a considerable inorganic fraction. Sample 1 contained light elements at 63.6%. The dominant inorganic elements were Si at 8.1%, Ca at 7.9%, Fe at 5.7%, Al at 3.0%, Pb at 2.7%, and Cl at 2.1%. Smaller amounts of Ti, Mg, S, Cu, Zn, P, Mn, Ba, Sb, Sr, Cr, and Ni were also detected.

Sample 2 showed a different elemental profile compared with Sample 1. The light element fraction was lower, at 33.3%, while the concentration of several inorganic elements was higher. The dominant elements in Sample 2 were Cu at 16.4%, Fe at 10.7%, Si at 9.1%, Ca at 8.0%, Pb at 6.73%, and Al at 5.5%. The high Cu and Pb contents indicate that this sample may have contained localised metallic contamination or particles.

Sample 3 contained light elements at 52.0%. The dominant inorganic elements were Si at 11.3%, Fe at 8.1%, Ca at 8.1%, Mg at 5.5%, Al at 4.9%, and Cl at 2.9%. Since Sample 3 was virgin PP, these inorganic elements are more likely related to additives, fillers, pigments, sample preparation, or ash-forming components rather than external river contamination.

The variation between Samples 1, 2, and 3 shows that the inorganic composition of the PP char samples was not uniform. This is expected for contaminated plastic material, where soil, sand, biofilm, organic residues, labels, pigments, and other foreign materials may be unevenly distributed on the plastic surface before pyrolysis. However, the presence of inorganic elements in the virgin PP reference also shows that inorganic residue can originate from the polymer material itself or from additives and processing-related components.

Sample 4 represented washed PP char. The light element fraction was 65.55%, and the dominant inorganic elements were Ca at 10.7%, Cl at 7.8%, Si at 5.8%, Fe at 2.6%, Al at 2.5%, and Mg at 2.0%. Compared with the dirty PP char samples, Sample 4 showed lower concentrations of several metallic elements, especially Cu, Pb, Zn, and Fe. This indicates that washing reduced part of the inorganic contamination before pyrolysis. However, the continued presence of Ca, Cl, Si, Fe, Al, and Mg shows that washing did not remove all inorganic residues.

## 9.3 XRF analysis of PE char products

Sample 5 represented dirty PE char from Aarhus River. The XRF analysis showed that the char contained light elements at 59.3% and a significant inorganic fraction. The dominant inorganic elements were Ca at 18.2%, Ti at 12.3%, Si at 3.5%, Cl at 2.0%, Al at 1.6%, and Fe at 1.4%. Smaller amounts of S, Ba, Zn, P, Mn, Cu, V, and other elements were also detected.



The high Ca and Ti contents suggest that Sample 5 contained inorganic mineral residues and/or additives such as fillers or pigments. Titanium may originate from titanium dioxide pigments, which are commonly used in plastics, while calcium may originate from mineral fillers, dirt, lime-containing particles, or contamination from the river environment. The presence of Cl may be related to salt, surface contamination, labels, additives, or other chlorine-containing residues.

Sample 6 represented virgin PE char. The XRF analysis showed that Sample 6 had the highest light element fraction of all samples, at 79.4%. The dominant inorganic elements were Si at 5.0%, Ca at 4.3%, Fe at 3.8%, Cl at 2.1%, Al at 2.0%, and Ti at 1.4%. Smaller amounts of Mg, P, S, Zn, Cr, Mn, Ba, and other elements were also detected.

Compared with Sample 5, Sample 6 contained much lower levels of Ca and Ti. This indicates that the contaminated Aarhus River PE contained more inorganic mineral or pigment-related residue than the virgin PE reference. However, the presence of Si, Ca, Fe, Cl, Al, and Ti in Sample 6 shows that even the virgin PE reference produced a char residue containing measurable inorganic components, possibly originating from additives, fillers, pigments, processing residues, or sample preparation.

## 9.4 Comparison and interpretation

The XRF results show clear differences between the PP and PE char samples. Samples 1–4 contained varying levels of Si, Ca, Fe, Al, Mg, Cl, Pb, Cu, Zn, and S, while Sample 5 was especially characterised by high Ca and Ti contents. Sample 6, the virgin PE reference, showed a higher light element fraction and lower levels of Ca and Ti compared with Sample 5. This indicates that the inorganic residue depends strongly on the original plastic fraction and the type of contamination, additives, fillers, or pigments associated with that fraction.

The PP char samples showed large variation in inorganic composition. Sample 2 was particularly different due to its high Cu, Fe, and Pb contents. This suggests that the char samples were heterogeneous and that inorganic particles were unevenly distributed. Therefore, the individual XRF measurements should not be interpreted as fully representative of the entire material batch without considering sample heterogeneity.

Sample 4, the washed PP char, contained lower amounts of several metallic elements compared with the dirty PP char samples. This indicates that washing had a positive effect on reducing part of the inorganic contamination. However, washing did not completely remove inorganic residues, as Ca, Cl, Si, Fe, Al, Mg, S, and P were still detected. Some inorganic material may therefore be strongly attached to the plastic surface, embedded in the material, or present as additives or fillers.

Compared with the PP char samples, Sample 5 contained lower Fe, Pb, Cu, and Zn, but considerably higher Ca and Ti. This suggests that the dirty PE fraction may contain more mineral filler or pigment-related material, whereas the PP samples appear to contain more variable external contamination. Compared with Sample 5, Sample 6 contained lower inorganic element concentrations and a higher light element fraction, which is consistent with its role as a cleaner PE reference material.

Overall, the comparison between Sample 5 and Sample 6 indicates that contamination from the river-collected PE fraction influenced the inorganic composition of the char. However, the presence of inorganic elements in Sample 6 also shows that clean reference materials can still leave measurable inorganic residues after pyrolysis.

## 9.5 Summary XRF

The XRF analysis showed that the char products contained measurable inorganic residues after pyrolysis. The PP char samples contained Si, Ca, Fe, Al, Mg, Cl, Pb, Cu, Zn, S, and other minor elements, with large variation between the samples.

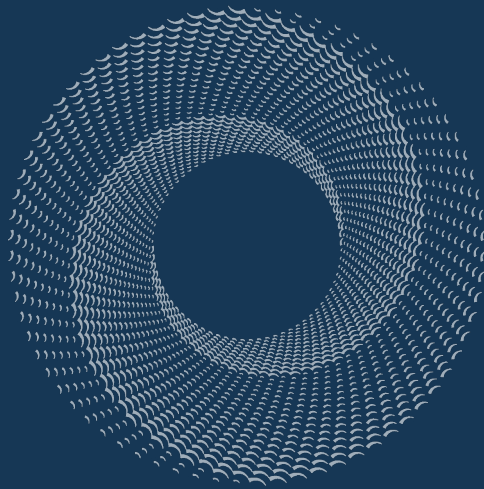
Sample 4 showed reduced levels of several metallic contaminants compared with the dirty PP char samples, indicating that washing had a positive effect, although inorganic residues were still present.

The PE char samples showed clear differences between contaminated Aarhus River PE and virgin PE. Sample 5 was dominated by Ca and Ti, suggesting the presence of mineral residues, fillers, pigments, or other inorganic additives in the contaminated PE fraction. Sample 6 had a higher light element fraction and lower concentrations of Ca and Ti, which is consistent with its role as a cleaner reference material. However, Sample 6 still contained measurable inorganic elements such as Si, Ca, Fe, Cl, Al, and Ti.

Overall, the XRF results indicate that the solid residue/char from pyrolysis contains inorganic material originating from contamination, additives, fillers, pigments, or mineral particles. The results also show that pre-treatment such as washing can reduce some contamination, but not eliminate it completely. This should be considered when evaluating possible applications of the char product.



**10.**  
**TGA analysis of  
solid residue/char**





## 10. TGA analysis of solid residue/char

### 10.1 Purpose of TGA analysis

Thermogravimetric Analysis (TGA) was performed on the solid residue/char products obtained after pyrolysis of the PP- and PE samples. The purpose of the TGA analysis was to evaluate the thermal behaviour of the char fractions and to estimate the relative amount of volatile material, residual carbonaceous material and inorganic ash-forming components present in the solid residues.

During TGA, the sample mass is monitored as a function of temperature and time. A decrease in mass indicates the release of volatile compounds, decomposition of residual organic material, or oxidation/degradation of carbonaceous material. The remaining mass at high temperature can be associated with thermally stable inorganic material, mineral residues, fillers, pigments, metal oxides or other ash-forming components.

The TGA results were used together with FTIR and XRF to evaluate whether contamination, additives, fillers and inorganic residues were concentrated in the char fraction after pyrolysis.

### 10.2 TGA analysis of PP char products

The TGA curves for the PP char products from Samples 1–4 are shown in Figure 14. Samples 1 and 2 represent contaminated Aarhus River PP, Sample 3 represents virgin PP, and Sample 4 represents washed Aarhus River PP.



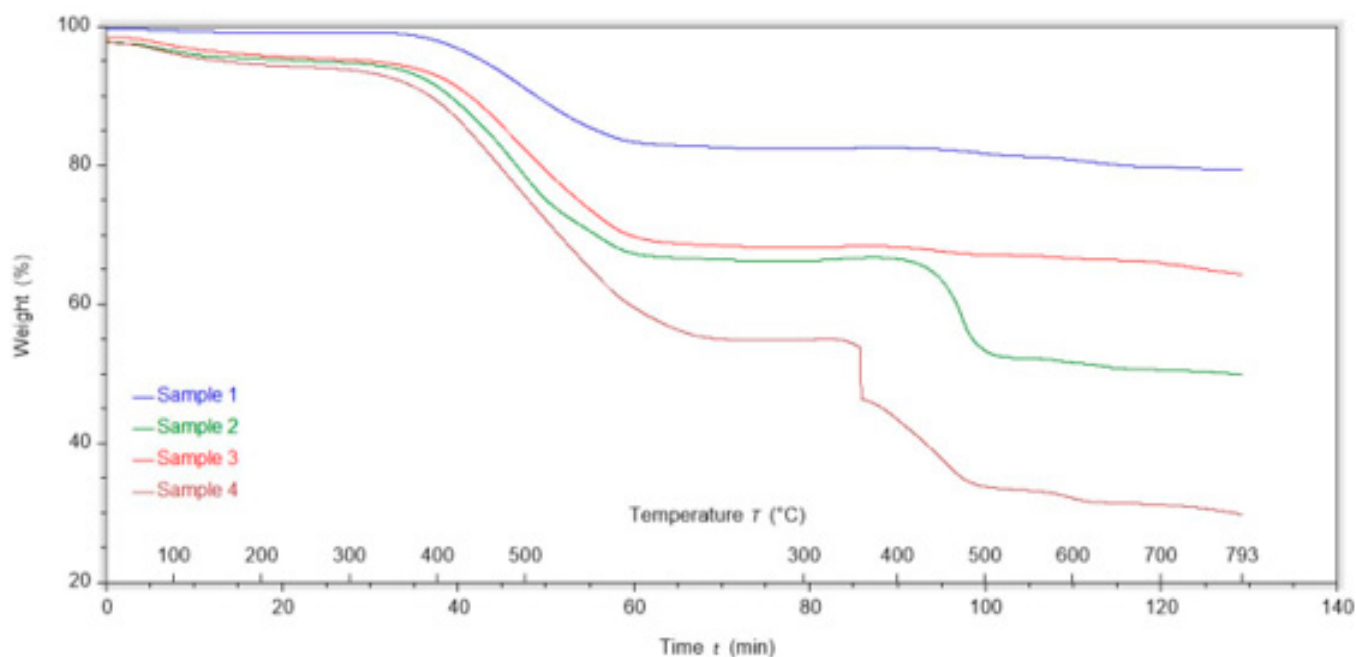


Fig. 14 TGA curves of char fractions from PP pyrolysis samples. Sample 1: contaminated Aarhus River PP, Sample 2: contaminated Aarhus River PP repeat, Sample 3: virgin PP, and Sample 4: washed Aarhus River PP.

All PP char samples showed a mass loss during heating, indicating that the solid residues still contained thermally degradable material. However, the extent of mass loss differed clearly between the samples.

Sample 1 showed the highest thermal stability among the PP char samples. The mass decreased only moderately during the first major degradation step and remained at approximately 79–80% at the end of the analysis. This indicates that Sample 1 contained a relatively high proportion of thermally stable residue. This may be related to inorganic material, ash-forming components, or less volatile carbonaceous material remaining in the char.

Samples 2 and 3 showed intermediate behaviour. Both samples lost more mass than Sample 1, but less than Sample 4. Sample 2 ended at approximately 49–50% remaining mass, while Sample 3 ended at approximately 64–65% remaining mass. The higher remaining mass of Sample 3 compared with Sample 2 indicates that the virgin PP char contained a larger fraction of thermally stable residue under the applied test conditions. However, the XRF results show that both samples contained inorganic elements, which may contribute to the final residue. Sample 4, the washed Aarhus River PP sample, showed the largest mass loss among the PP char samples. Its final remaining mass was approximately 29–30%. A clear mass loss occurred during the main heating stage, followed by an additional significant mass decrease at higher temperature. This suggests that the char from washed PP contained a higher proportion of thermally degradable residual organic or carbonaceous material compared with the other PP char samples.

Overall, the TGA results for the PP char samples show that the solid residues had different thermal behaviours. Sample 1 retained the highest mass after heating, while Sample 4 retained the lowest mass. These differences indicate variation in the relative amount of residual organic material, carbonaceous residue and inorganic ash-forming components between the PP char samples.

### 10.3 TGA analysis of PE char products

The TGA curves for the PE char products from Samples 5 and 6 are shown in Figure 15. Sample 5 represents contaminated Aarhus River PE, while Sample 6 represents virgin PE.'

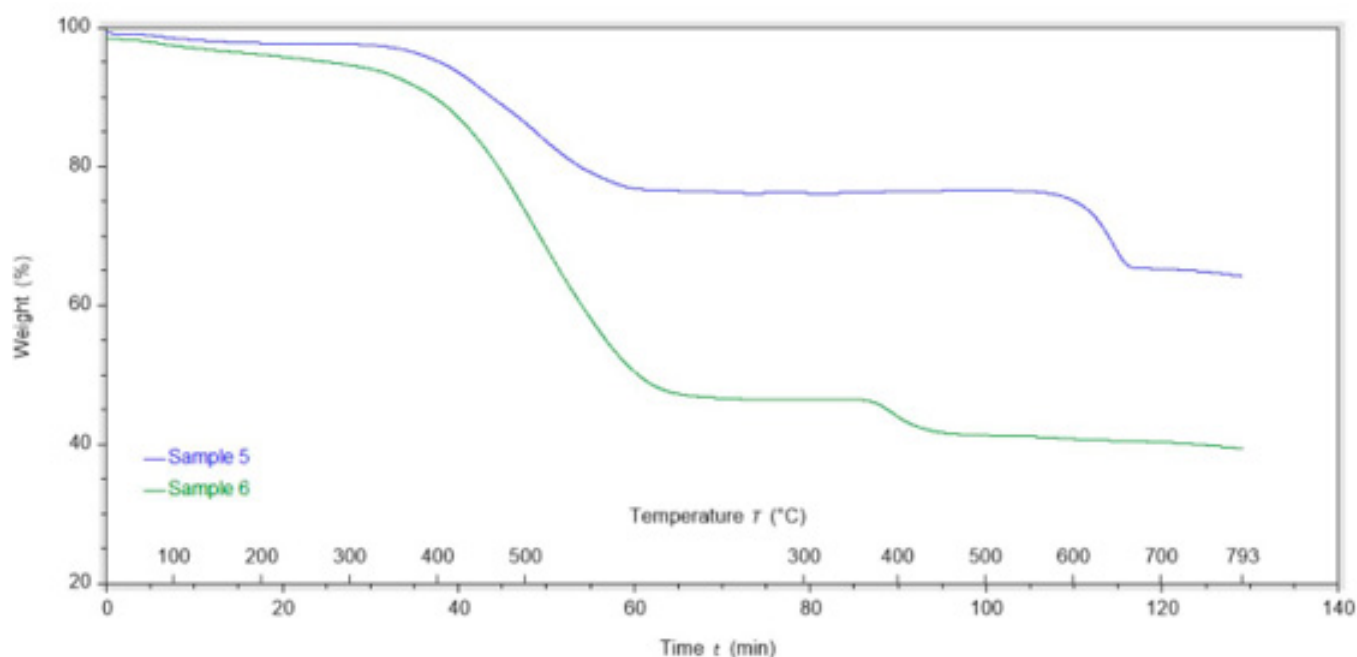


Fig. 15 TGA curves of char fractions from PE pyrolysis samples. Sample 5: contaminated Aarhus River PE, and Sample 6: virgin PE.

Both PE char samples showed mass loss during heating, but the behaviour of the two samples differed clearly. Sample 5 retained a higher mass throughout the analysis compared with Sample 6. At the end of the test, Sample 5 had approximately 64–65% remaining mass, while Sample 6 had approximately 39–40% remaining mass.

Sample 5 showed a moderate mass loss during the main degradation stage and retained a relatively high final residue. This indicates that the contaminated Aarhus River PE char contained a significant amount of thermally stable material. This is consistent with the XRF results, where Sample 5 showed high levels of calcium and titanium. These elements may originate from mineral particles, fillers, pigments, additives or other inorganic contamination associated with the river-collected PE fraction.

Sample 6, the virgin PE reference, showed a larger mass loss than Sample 5. The main degradation occurred during the heating stage, and the final remaining mass was lower. This suggests that the virgin

PE char contained a higher proportion of thermally degradable organic or carbonaceous material and a lower proportion of thermally stable inorganic residue compared with the contaminated PE char.

Overall, the TGA results for the PE char samples indicate that the contaminated Aarhus River PE char contained more thermally stable residue than the virgin PE char. This supports the interpretation from FTIR and XRF that inorganic material, fillers, pigments, additives or contamination were concentrated in the char fraction of the contaminated PE sample.

## 10.4 Comparison and interpretation

The TGA results show that all char samples contained both thermally degradable material and thermally stable residue. The mass losses observed during heating indicate that the char fractions still contained residual organic or carbonaceous material after pyrolysis. The remaining mass at high temperature indicates the presence of thermally stable ash-forming material, such as inorganic residues, mineral particles, fillers, pigments, metal oxides or other non-volatile components.

For the PP char samples, Sample 1 retained the highest final mass, while Sample 4 retained the lowest final mass. This indicates that the PP char products differed considerably in composition. The high remaining mass of Sample 1 may indicate a higher fraction of stable inorganic or carbonaceous residue. In contrast, the lower remaining mass of Sample 4 suggests that the washed PP char contained a larger proportion of thermally degradable material under the applied TGA conditions.

For the PE char samples, Sample 5 retained considerably more mass than Sample 6. This indicates that the contaminated Aarhus River PE char contained more thermally stable material than the virgin PE char. This is consistent with the XRF results, where Sample 5 showed high levels of calcium and titanium, which may be associated with mineral residues, fillers, pigments or contamination.

The TGA results support the conclusions from FTIR and XRF. FTIR showed that the char and ashed char samples contained broad absorption features related to inorganic or mineral-like structures, while XRF confirmed the presence of inorganic elements in all char samples. TGA further shows that part of the char residue remained stable at high temperature, supporting that inorganic and ash-forming components were retained in the solid fraction after pyrolysis.

Overall, the combined interpretation indicates that pyrolysis transferred the main polymer-derived hydrocarbons into the oil/wax fraction, while inorganic residues, fillers, pigments, additives and contamination were mainly concentrated in the char/ash fraction.

## 10.5 Summary TGA

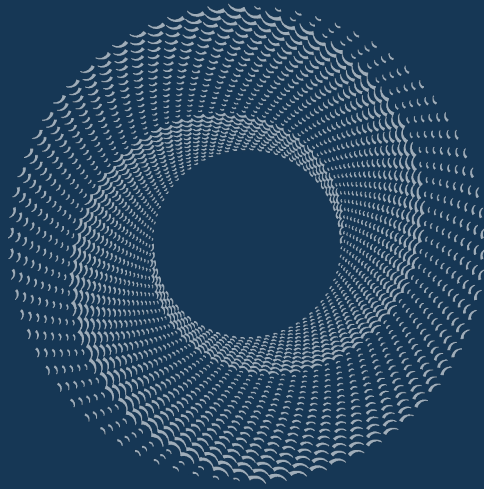
TGA analysis was used to evaluate the thermal behaviour of the solid residue/char products from the PP- and PE pyrolysis samples. All char samples showed mass loss during heating, indicating the presence of residual thermally degradable organic or carbonaceous material. At the same time, all samples retained a measurable final residue, indicating the presence of thermally stable ash-forming components.

For the PP char samples, the final remaining mass varied considerably. Sample 1 retained the highest mass, while Sample 4 retained the lowest mass. This shows that the PP char samples differed in the relative amount of thermally degradable material and stable residue.

For the PE char samples, Sample 5 retained a higher final mass than Sample 6. This indicates that the contaminated Aarhus River PE char contained a higher proportion of thermally stable residue than the virgin PE reference. This is consistent with the XRF results, where Sample 5 contained high levels of calcium and titanium.

Overall, the TGA results support the FTIR and XRF findings. The char fractions contained residual carbonaceous material together with inorganic or ash-forming components. The results indicate that contamination, fillers, pigments, additives and mineral residues were mainly retained in the solid char/ash fraction after pyrolysis rather than being transferred into the oil/wax products.

# 11. Discussion





## 11. Discussion

The results from the six pyrolysis reactions show that pyrolysis can convert selected PP and PE fractions from the Aarhus River OBP stream into condensable oil/wax products, non-condensable gas and a minor solid char fraction. For most samples, the oil/wax fraction was the dominant collected product, while char formation remained low for all samples. The char yield ranged from 0.1% to 1.5%, showing that only a small fraction of the input material remained as solid residue after pyrolysis. However, the distribution between oil/wax and gas varied between polymer types and sample conditions, especially for the PE samples.

For the PP samples, the oil/wax yields were relatively high and ranged from 66.4% to 79.5%. Samples 1 and 2, both contaminated Aarhus River PP, gave very similar oil/wax yields of 79.5% and 78.9%, respectively. This indicates good repeatability between the two contaminated PP pyrolysis reactions. The washed Aarhus River PP sample, Sample 4, produced an oil/wax yield of 73.1%, while the virgin PP reference, Sample 3, produced an oil/wax yield of 66.4%. These results suggest that the contaminated and washed Aarhus River PP fractions were suitable for conversion into oil/wax under the applied pyrolysis conditions. The low char yields for all PP samples indicate that solid residue formation was limited, even for the contaminated river-collected material.

The PE samples showed a more pronounced difference between contaminated and virgin material. Sample 5, contaminated Aarhus River PE, produced the lowest oil/wax yield, 37.6%, and the highest gas fraction, 60.9%. In contrast, Sample 6, virgin PE blend, produced the highest oil/wax yield of all samples, 86.2%, and the lowest gas fraction, 13.6%. This indicates that the contaminated PE fraction behaved differently from the clean PE reference during pyrolysis. The higher gas fraction for Sample 5 may be related to contamination, mixed material composition, moisture, additives, degradation state or process behaviour during the experiment. Because the gas phase was not collected or analysed directly, this fraction should be interpreted as gas rather than as a pure gas yield.

The TAN results show that sample condition influenced the acidity of the oil/wax products. The highest TAN value was measured for Sample 1, contaminated Aarhus River PP, with an average value of 4.2 mg KOH/g oil. Sample 2, which was also contaminated Aarhus River PP, had a lower TAN value of 1.3 mg KOH/g oil. The virgin PP reference and washed PP sample had lower TAN values of 0.5 and 0.4 mg KOH/g oil, respectively. This suggests that contamination, degradation products or oxygen-containing compounds associated with the river-collected material may have contributed to increased acidity in the PP-derived oil/wax products. The lower TAN value for the washed PP sample indicates that washing may reduce part of the contamination-related contribution, although it did

not remove all differences between the river-collected and virgin samples.

For the PE-derived oil/wax products, the TAN values were generally low. Sample 5, contaminated PE, had an average TAN value of 0.4 mg KOH/g oil, while Sample 6, virgin PE, had the lowest value of 0.2 mg KOH/g oil. This indicates that the PE-derived oil/wax products contained relatively low amounts of acidic compounds compared with the contaminated PP samples.

The slightly higher TAN value for contaminated PE compared with virgin PE may still suggest a minor effect of contamination or degradation products, but the difference was much smaller than observed for the PP samples.

The FTIR results showed that the oil/wax products from the PP samples were chemically similar. Samples 1–4 all showed strong aliphatic C–H stretching bands, CH<sub>2</sub> and CH<sub>3</sub> bending vibrations, and bands related to unsaturated hydrocarbon structures. This indicates that the PP-derived oil/wax products were mainly composed of aliphatic and unsaturated hydrocarbons formed during thermal cracking of polypropylene. The close similarity between contaminated, washed and virgin PP oil/wax spectra suggests that contamination and washing did not strongly change the main hydrocarbon character of the PP-derived oil/wax fraction.

The PE-derived oil/wax products also showed characteristic hydrocarbon structures in FTIR. Samples 5 and 6 were dominated by long-chain aliphatic hydrocarbon bands, including CH<sub>2</sub> stretching, CH<sub>2</sub> bending and CH<sub>2</sub> rocking vibrations. These results are consistent with PE-derived pyrolysis products containing linear hydrocarbon structures. Although the contaminated PE sample showed a very different product yield distribution compared with the virgin PE reference, the FTIR results indicate that the main oil/wax product still had a hydrocarbon character consistent with polyethylene degradation.

The GC-MS results supported the FTIR interpretation and showed that the oil/wax composition was mainly governed by polymer type. The PP-derived oil/wax products contained branched, cyclic and unsaturated hydrocarbons, while the PE-derived oil/wax products were mainly composed of linear alkanes and alkenes. This difference is consistent with the expected degradation behaviour of PP and PE. Overall, FTIR and GC-MS did not indicate major changes in the main organic character of the oil/wax products caused by contamination. However, these methods mainly describe the organic composition of the oil/wax fraction and should not be used alone to prove the complete absence of inorganic contamination in the oil/wax products.

The char and ash analyses provided additional information about contamination and inorganic

residues. FTIR analysis of the char samples showed weaker hydrocarbon-related bands compared with the oil/wax products and stronger contributions from oxygen-containing and mineral-related structures. After ashing, the hydrocarbon-related features were reduced, while broad mineral-related absorption regions became more dominant. This indicates that the remaining ashed material contained inorganic or mineral-like residues.

The XRF results showed that the char fractions contained inorganic elements such as calcium, silicon, iron, aluminium, chlorine and other elements associated with mineral residues, pigments, additives, labels, dirt or other contamination sources. Contaminated river-collected samples generally showed evidence of inorganic residues in the char fraction. The TGA results also supported the presence of thermally stable ash-forming material in the solid residues. Together, the FTIR, XRF and TGA results indicate that inorganic elements and thermally stable ash-forming material appeared to be mainly retained in the solid char/ash fraction.

It should be noted that the presence of inorganic residue was not only observed in contaminated river-collected samples. Some inorganic or ash-forming residue was also observed in reference materials. This may originate from fillers, additives, sample preparation, trace contamination or minor inorganic components in the material, rather than only from river-collected contamination. Therefore, differences between contaminated, washed and virgin samples should be interpreted carefully and in relation to all analytical results.

Overall, the results show that polymer type had a strong influence on the chemical character of the oil/wax products, while contamination and washing mainly affected product yield, acidity and solid residue composition. For the PP samples, contaminated and washed Aarhus River PP produced oil/wax products that were chemically comparable in their main hydrocarbon character to the virgin PP reference, although the contaminated PP samples showed higher TAN values. For the PE samples, contamination had a stronger effect on the mass balance, especially by reducing oil/wax yield and increasing the gas/loss fraction. However, the main organic character of the PE-derived oil/wax product remained consistent with PE pyrolysis products.

These findings suggest that pyrolysis could potentially be a relevant complementary recycling route for selected PP and PE fractions from the Aarhus River OBP stream, especially for material fractions that are difficult to recycle mechanically. Washing and pre-treatment remain important because they may improve product quality, reduce acidity and limit contamination-related residues. However, the collected oil/wax products were complex, unfractionated mixtures containing a broad range of hydrocarbons rather than clean, separated product streams. Therefore, substantial further

work is still required before these products could be considered suitable for specific downstream applications. Improved condensation, staged fractionation, distillation and possible upgrading or blending would be needed to separate lighter and heavier components, improve consistency and obtain products with more clearly defined quality.

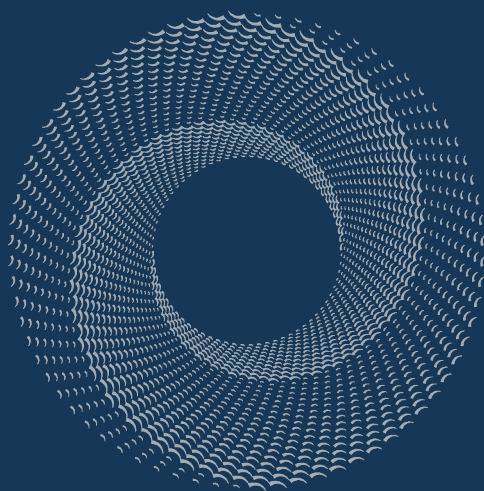
Thus, while untreated polyolefin-rich OBP fractions can produce oil/wax products with a hydrocarbon character broadly comparable to clean reference materials, the present process should be regarded as an initial conversion step rather than a route that directly produces clean, ready-to-use products.







# 12. Conclusion



## 12. Conclusion

This study investigated pyrolysis as a chemical recycling route for selected polypropylene (PP) and polyethylene (PE) fractions of ocean-bound plastic (OBP) collected from Aarhus River. Contaminated, washed and virgin reference samples were included in order to evaluate how polymer type, contamination and washing influenced product yield, oil/wax quality and solid residue composition.

Across the six pyrolysis reactions, the oil/wax fraction was the dominant collected product for most samples, while char formation remained consistently low, ranging from 0.1% to 1.5%. For the PP samples, the oil/wax yields were relatively high and ranged from 66.4% to 79.5%. The two contaminated Aarhus River PP samples produced very similar oil/wax yields, indicating good repeatability between the two contaminated PP pyrolysis reactions. The washed Aarhus River PP sample also produced a high oil/wax yield, while the virgin PP reference showed a slightly lower oil/wax yield under the applied conditions.

The PE samples showed a more pronounced difference between contaminated and virgin material. The contaminated Aarhus River PE sample produced a much lower oil/wax yield and a much higher gas fraction than the virgin PE reference blend. This indicates that the contaminated PE fraction behaved differently during pyrolysis and that contamination, mixed material composition, moisture, additives or process behaviour may have influenced the product distribution. Since the gas phase was not collected or analysed directly, this fraction should be interpreted as gas rather than as a pure gas yield.

The TAN results showed that the acidity of the oil/wax products varied between the samples. The contaminated PP samples showed higher TAN values than the virgin and washed PP samples, especially Sample 1. This suggests that contamination, degradation products or oxygen-containing compounds may have contributed to increased oil acidity. Washing appeared to reduce the TAN value for the Aarhus River PP sample, indicating that pre-treatment may improve oil/wax quality, although it did not remove all contamination-related effects. The PE-derived oil/wax products had relatively low TAN values compared with the contaminated PP samples.

FTIR and GC-MS analyses showed that the chemical character of the oil/wax products was mainly governed by polymer type. The PP-derived oil/wax products were dominated by branched, cyclic and unsaturated hydrocarbons, while the PE-derived oil/wax products were mainly composed of linear alkanes and alkenes. Contamination and washing did not appear to strongly change the main hydrocarbon character of the oil/wax products, although contamination affected yield, gas formation

and, for PP, oil acidity. The main findings from the different analyses are summarized in Table 7.

Table 7 Overall summary of the main results from the pyrolysis study.

| Analysis/result area           | Main conclusion                                                                                                                                                                                                                                                                              |
|--------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Product yield and mass balance | Oil/wax was the dominant collected product for most samples. Char formation was low for all samples, ranging from 0.1% to 1.5%. The contaminated PE sample showed the largest deviation, with low oil/wax yield and high gas fraction.                                                       |
| Density                        | The oil/wax products had densities between 0.71 and 0.81 g/mL. The values were generally comparable, but differences indicate variation in product composition, wax content and light/heavy hydrocarbon fractions.                                                                           |
| Total acid number (TAN)        | Contaminated PP showed higher acidity than virgin and washed PP, especially Sample 1. Washing reduced the TAN value, suggesting that pre-treatment can reduce contamination-related acidity. PE-derived oil/wax products had relatively low TAN values.                                      |
| FTIR oil/wax                   | FTIR showed that the oil/wax products were dominated by hydrocarbon structures. PP-derived products showed aliphatic and unsaturated hydrocarbon bands, while PE-derived products showed long-chain aliphatic hydrocarbon structures.                                                        |
| GC-MS oil/wax                  | GC-MS confirmed that the oil/wax composition was mainly governed by polymer type. PP products contained branched, cyclic and unsaturated hydrocarbons, while PE products were mainly composed of linear alkanes and alkenes                                                                  |
| FTIR char/ash                  | Char spectra showed weaker hydrocarbon bands and stronger oxygen-containing and mineral-related features compared with the oil/wax products. Ashed char spectra indicated that inorganic/mineral residues remained after removal of organic material.                                        |
| XRF char                       | XRF showed that the char contained inorganic elements such as Ca, Si, Fe, Al, Cl and other contamination-related elements. This indicates that inorganic contamination was mainly retained in the solid residue.                                                                             |
| TGA char                       | TGA showed differences in thermal behaviour and residual ash content between samples. Higher ash residues in contaminated samples supported the presence of inorganic or ash-forming material in the char fraction.                                                                          |
| Overall interpretation         | Pyrolysis appears to be a relevant complementary recycling route for selected PP and PE OBP fractions. The oil/wax products from contaminated material were chemically comparable to those from virgin references, although contamination affected yield, TAN and solid residue composition. |

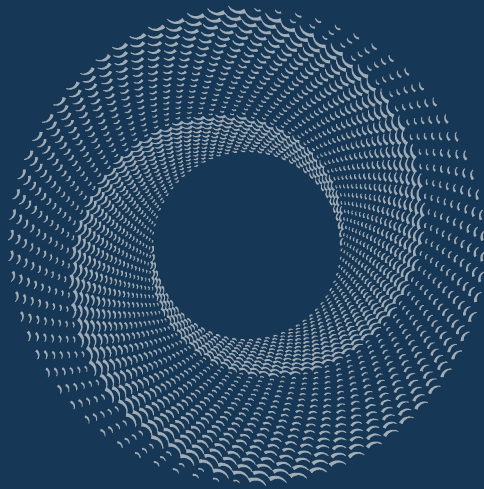
The FTIR, XRF and TGA results for the solid residues indicate that inorganic and ash-forming material was mainly retained in the char/ash fraction. The char samples contained weaker hydrocarbon-related FTIR bands and stronger oxygen-containing or mineral-related features compared with the oil/wax products. XRF identified inorganic elements such as calcium, silicon, iron, aluminium and chlorine in the char fractions, while TGA showed differences in thermal behaviour and residual ash content. Together, these results suggest that char and ash analysis is important for evaluating contamination and inorganic residues in pyrolysis of OBP materials.

Overall, the results show that pyrolysis is a technically relevant complementary recycling route for selected PP and PE fractions from the Aarhus River OBP stream, especially for material fractions that

are difficult to recycle mechanically. The oil/wax products from river-collected material were broadly comparable in hydrocarbon character to those obtained from virgin reference polymers, although contamination influenced product yield, gas formation, TAN values and solid residue composition. Pre-treatment such as washing is therefore recommended when possible, as it may improve oil/wax quality and reduce contamination-related effects. However, the results also indicate that untreated polyolefin-rich OBP fractions can still produce oil/wax products with a hydrocarbon character similar to clean reference materials.

# 13.

## Recommendations





## 13. Recommendations

Based on the results and conclusions of this study, the following recommendations are proposed for future work and for the potential development of pyrolysis as a recycling route for OBP fractions:

### 1. Test a washed PE sample.

This study included a washed PP sample but no equivalent washed PE sample. Given that contamination had a more pronounced effect on PE yield and gas than on PP, testing a washed contaminated PE fraction would clarify whether washing can similarly mitigate the yield loss observed for Sample 5.

### 2. Increase repeatability for PE and washed PP conditions.

The PP test series included two repeat reactions on contaminated material (Samples 1 and 2), which showed good repeatability and strengthened confidence in those results. The PE and washed-PP conditions were each represented by only a single reaction. Repeating these conditions would help confirm whether the observed differences (e.g., the low oil/wax yield for contaminated PE) are representative or specific to that individual run.

### 3. Investigate the cause of reduced PE oil/wax yield.

The substantially lower oil/wax yield and higher gas fraction for contaminated PE compared with virgin PE was the most pronounced effect seen in this study. Further work could investigate whether this is driven by the LDPE/HDPE ratio, specific contaminants, moisture content, or reactor/process conditions, since this has a direct bearing on the economic viability of pyrolysing contaminated PE at scale.

### 4. Evaluate upgrading or blending strategies for the oil/wax product.

Although the oil/wax products were chemically similar to virgin-derived material, the elevated TAN values in contaminated PP oil/wax (particularly Sample 1) indicate a higher acid content that could affect downstream use or storage. Options such as mild post-treatment, neutralisation, or blending with lower-TAN oil/wax fractions could be explored to improve product consistency.

### 5. Assess the fate and value of the char/ash fraction.

XRF and TGA results indicated that contamination-related inorganic material was mainly retained in the char rather than being evident in the oil/wax product. Since this fraction consistently contains calcium, titanium, silicon and iron, it may be worth evaluating whether the char has any secondary value (e.g., as a filler or mineral-recovery stream) or whether it requires specific handling as a waste fraction.

## **6. Investigate the relationship between feed mass and reactor volume.**

The ratio between the mass of plastic introduced and the available reactor volume should be investigated systematically. Sufficient free volume is needed to allow the material to move and mix effectively during heating, support more uniform heat transfer, and reduce the risk of local overheating or incomplete conversion. Overfilling the reactor may restrict movement of the material and limit contact with the heated surfaces, which could influence oil/wax yield, gas/loss formation and char production. Future experiments should therefore evaluate different reactor loading levels and determine an appropriate feed mass-to-reactor volume ratio for each material type and physical form.

## **7. Scale-up and continuous-process considerations.**

This study was performed using a batch reactor at laboratory scale. Before pyrolysis can be considered a viable complementary recycling route in practice, further work should address how yield, product quality, and contamination effects translate to a continuous or larger-scale process, including the practical implications of feedstock variability in real OBP streams.

## **8. Improve condensation and fraction separation.**

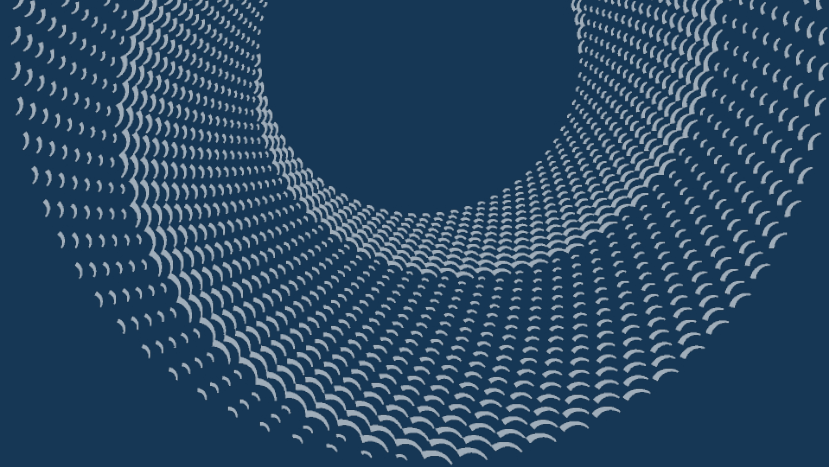
In the present study, the condensable products were collected as a combined oil/wax fraction, and no subsequent distillation was performed. The existing condensation system did not allow clear separation into lighter and heavier product fractions. Future work should therefore investigate the use of additional condensers, staged condensation or downstream distillation to achieve better separation of volatile oil, heavier oil and wax fractions. Improved fractionation would support more detailed product characterisation and could make it easier to identify suitable downstream applications for each fraction.

## **9. Evaluate lower condensation temperatures.**

The efficiency of vapour recovery may be improved by operating the condensation system at lower temperatures. Future experiments could investigate cooling with ice water or dry ice, depending on the required temperature range and equipment compatibility. Lower condensation temperatures may improve recovery of lighter volatile compounds that could otherwise remain in the non-condensable gas/loss fraction. However, the cooling method should be selected carefully to avoid blockage caused by rapid wax solidification and to ensure safe and stable operation.







# Circular Ocean-bound Plastic

Breaking the waves of ocean plastic pollution  
- From source to solution

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