

Storage Stability of Plastics Pyrolysis Oils from Post-Consumer Polyolefin Waste

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Abstract

This study investigates the influence of storage temperature and heteroatom content on the physicochemical stability and property variations of pyrolysis oils.

Virgin polyolefins and commercially available pre-treated mixed polyolefin waste were pyrolyzed in a pilot-scale screw reactor. The resulting oils were stored at ambient temperature and 60 °C for up to eight weeks. Changes in their chemical composition and physical properties were monitored using GC-FID, GCxGC-MS/FID-NCD, NMR, and viscosimetry, across multiple time scales. Within the first days of storage, small amounts of a highly viscous, bitumen-like phase formed in the samples with elevated levels of heteroatoms stored at ambient temperature. No viscous phase formation was observed in the oil from virgin polymers. Pyrolysis oils showed no changes in hydrocarbon composition throughout the evaluated storage period, neither at room temperature nor at 60 °C. We therefore argue that storage stability of plastics-derived pyrolysis oils is a multifaceted phenomenon.

This systematic study highlights the crucial role of heteroatom contamination in the degradation processes. These insights into the processes during storage can inform mitigation strategies against degradation. Improving the storage stability of plastics-derived pyrolysis oils represents a significant step towards the implementation of chemical recycling at industrial scale.

Table 1. List of Abbreviations

Abbreviation	Meaning
ABS	Acrylonitrile-Butadiene-Styrene Copolymer
PA6	Polyamide-6
PCW	Post-Consumer Plastic Waste
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PPO	Plastics-derived pyrolysis oil
RT	Room temperature

Introduction

Plastics are a versatile group of materials and among the most produced man-made materials [1,2]. As production and use of plastics have increased, so has the generation of plastic waste [2]. It is estimated that, at the global level, 46 % of this waste is being landfilled, 17 % incinerated, 15 % recycled and around 20 % mismanaged, which includes littering and informal dumping into the environment [3]. Landfilling, incineration, and mismanagement are not considered sustainable practices each for their own reasons [4–6]. Recycling can reduce environmental burdens, if the products from recycling substitute products produced from primary raw materials effectively [7–9].

Plastic recycling routes are commonly categorized as either *chemical* or *mechanical recycling* [10,11]. While mechanical recycling aims to preserve the chemical structure of the plastics, chemical recycling deliberately breaks down the polymers into monomers or other small fragments [10]. Mechanical recycling relies on sophisticated collection and sorting systems to achieve high-purity input, however, the applicability of recyclates can be limited. Chemical recycling can treat more diverse and impure waste streams that are not suitable for mechanical recycling, this includes residual streams from

mechanical recycling plants [10,12]. Therefore, it should be viewed as a complementary recycling pathway to mechanical recycling [12,13].

Among chemical recycling processes, pyrolysis has received much attention, as it enables diverse mixed plastic waste streams to be processed [10,14]. Pyrolysis employs temperatures of between 300 and 700 °C and an inert gas atmosphere to break down the polymers, typically yielding a solid residue of char and inorganics as well as a wide range of volatile hydrocarbon molecules [12].

Pyrolysis also has the potential to process mixed plastic feedstocks and contaminated post-consumer plastic waste (PCW), such as multilayer packaging [10], waste from end-of-life automobiles and electronic devices [15]. However, the composition of the pyrolysis oils depends on the composition of the feedstock [16]. In particular, contaminant elements, i.e. elements other than carbon and hydrogen, such as chlorine, bromine, nitrogen or metals, contained in the feedstock, can end up in the oil, limiting its use for certain applications, such as steam cracking [17].

Ageing of hydrocarbon mixtures

Research on the storage properties and stability of plastics-derived pyrolysis oils (PPO) is scarce [18]. In most cases, the investigation comprises only one kind of oil and one type of storage conditions. For example, Kusenberget al. [19] found that small amounts of particulate contamination are generated during storage of PPO from one sorted PO-rich PCW over two days. They also found that the elemental composition of the particles generated during ageing contained a higher share of oxygen and silicon (among others) than the particles from the pyrolysis process.

Faussone et al. [20] stored pyrolysis oil from PCW rich in PE and PP for five years and compared it to fresh PPO and to PPO that had been stored for six months. GC-MS analysis revealed that longer chains had formed over time, which were not originally found in the pyrolysis oil. Simulated distillation showed that the boiling curve had shifted markedly towards higher boiling points. However, as the evolution over time is not shown, the timeframe of ageing remains uncertain.

Fekhar et al. [18] examined the ageing of pyrolysis oils obtained from in-situ catalytic and thermal pyrolysis of post-consumer plastic waste rich in PE and PP. The oils were aged at 80°C for 7 days. The density, viscosity, total acid number (TAN), iodine number and formation of an “oligomer-polymer phase” were tracked over time. PPO obtained without catalyst, which contained less aromatics and more paraffins and olefins, showed clearer signs of aging in terms of TAN and the amount of “oligomer-polymer phase”. They suggested that olefinic hydrocarbons may react to form this phase.

While research on the ageing behavior of pyrolysis oils from biogenic feedstocks is abundant by comparison (see e.g. [21]), plastics, especially polyolefins, are chemically more closely related to high-molecular hydrocarbons, which could be found in crude oils or other petroleum products [16]. The stability of fuels, especially from both catalytic and thermal cracking of such feedstocks, has been a matter of concern for some time [22–25].

Nagpal et al. [22], e.g., found that olefins play an important role in the formation of gum in gasoline. Gum is a general term for non-volatile products formed in gasoline and other hydrocarbon fuels [24]. Nagpal et al. later detailed that cyclic olefins and conjugated diolefins promote the formation of gum remarkably more than linear olefins [26]. This was confirmed by Pereira and Pasa [27]. They attributed this effect to the stability of the formed radicals in a chain reaction mechanism based on the oxidation of C=C double bonds through peroxide formation.

Additional mechanisms for polymerization, such as acid-base or esterification reactions of multi-functional compounds, have been discussed as a potential source for deposits [23,28]. Often, it was found that not one single compound or compound class was responsible for sediment or gum formation, but rather the synergy of different compounds.

Experimental

Pyrolysis conditions and feedstock

Pyrolysis was conducted in a pilot-scale trough screw reactor, which has been previously described in detail [15,29,30]. 1 kg h⁻¹ of feedstock and 4 kg h⁻¹ of quartz sand were fed continuously into the reactor, which operated at a solids residence time of 30 minutes to achieve complete conversion. The total quantity of pyrolysis oil from one day’s experiment was divided into two batches: one stored in a drying oven at 60°C and the other stored at room temperature. Both batches were kept in the dark, with the flask headspace filled with nitrogen to prevent reactions with elemental oxygen.

The feedstocks for pyrolysis were, firstly, a mixture of virgin PP and LDPE granulate, in the proportions of 70 wt% PP to 30 wt% LDPE. Secondly, a commercially available pre-processed post-consumer plastic waste PCW agglomerate, sorted to contain at least 95 wt% polyolefin was used. Thirdly, the same PCW agglomerate was mixed with shredded standard printer paper at a ratio of 95 wt% PCW to 5 wt% paper, reducing the minimum polyolefin content to around 90 wt%.

Sample analysis

Samples were first analyzed as soon as possible after oil generation, followed by a series of analyses after 2, 7, 22, and 57 days. Viscosity, GC-FID, and NMR measurements were performed at each interval. In addition, elemental analysis and GCxGC as well as density measurements were performed once before the storage period for each oil.

Viscosity of the samples was measured using a *Thermo Scientific* HAAKE falling-sphere viscometer conforming to DIN 53015 held at 60°C. Density measurements were taken using a standard hydrometer with 0.002 kg/m³ precision. Elemental analysis was performed using a *LECO* Truspec CHN Micro. Chlorine and Bromine were determined separately via combustion ion chromatography (C-IC) using an *A1 Environscience* AQF-2100.

Functional structure analysis by proton nuclear magnetic resonance spectroscopy (¹H NMR) was carried out using a *Magritek* SpinSolve 80 Ultra benchtop spectrometer. TMS was used as the internal reference.

GC-FID

To investigate the effects of storage conditions, gas chromatography with flame ionization detection (GC-FID) was employed. The analytical approach closely resembles the principles of simulated distillation, enabling the characterization of hydrocarbon distributions across a wide boiling range.

Analyses were performed using a non-polar capillary column (MXT-1, 15 m × 0.25 mm i.d., 0.1 µm film thickness). The temperature program was set as follows: initial temperature at 35 °C, followed by a ramp of 4.5 °C/min to 300 °C and 6 °C/min to 390 °C, with a final hold of 6 min. The injector and detector temperatures were maintained at 350 °C and 420 °C, and helium was used as the carrier gas.

The analysis primarily focused on the relative abundances of organic constituents with respect to the carbon chain length of n-alkanes. Calibration was performed using a homologous series of n-alkane standards to assign carbon numbers to individual peak groups. This approach allowed for the assessment of compositional shifts and potential degradation pathways during storage.

GCxGC

The 2-dimensional gas chromatography (GCxGC) setup and quantification method followed Ref. [31]. The GCxGC uses a normal-phase column setup, joined to a three-way splitter, which distributes the flow between a QMS and a tandem FID-NCD detector according to a volume ratio of 1:10. Quantification of non-calibrated compounds is based on group analysis. The sample was dissolved in chromatography-grade chloroform to yield a concentration of 75 – 90 mg/ml.

Results and Discussion

Initial Oil Characterization

Elemental analysis

Elemental analyses of the PPO from the experiments are presented in Table 2 and Table 3. All three oils have equal proportions of carbon and hydrogen, as well as residual mass, assumed to be oxygen. H:C-ratio was 1.83 for the oil from virgin polyolefins and 1.79 for both PCW-derived oils. For the oil from virgin feedstock, nitrogen content was below quantification limit of 0.2 wt% and for the PCW-derived oils slightly higher at 0.3 wt%. Oxygen content ranged within measurement error at 0.1 – 0.2 wt%.

Addition of 5 % by weight of paper to the feedstock did not impact the elemental composition meaningfully – this could be due to the uncertainty from determining oxygen content by difference. Typical products from the pyrolysis of cellulose, could not be detected in GCxGC analysis either (see below). Other oxygenated species, could be found in both the oil derived from PCW and the oil derived from PCW + paper in equal concentration.

Bromine content was below 30 ppmw for all oils, while chlorine was below 30 ppmw only for the PPO from virgin feedstock. Addition of paper to the PCW feedstock did not change chlorine content in the oil from 82 ppmw significantly.

As the viscous phase accumulated heteroatoms and formed very quickly (for more details see Viscous phase Formation & Analysis section), it is possible that the heteroatom content of the oils at the beginning is underestimated, due to time delay from sample transport.

Table 2. Elemental analysis of Oils and Viscous Phases – CHN /O

in wt%	C		H		N		Residual / O
<i>Oils</i>							
Virgin PP + PE	86,6	± 1,5	13,2	± 0,2	< 0,2 ^a		0,2
PCW	86,6	± 1,3	12,9	± 0,2	0,32	± 0,02	0,1
PCW + Paper	86,6	± 1,5	12,9	± 0,1	0,29	± 0,01	0,2
<i>Viscous phase^b</i>							
PCW	72,3	± 0,6	8,30	± 0,2	6,89	± 0,6	11,7
PCW (60°C)	69,0	± 1,0	8,97	± 0,5	6,00	± 1,3	15,4
PCW + Paper	65,8	± 1,0	8,32	± 0,4	5,30	± 0,6	19,7
PCW + Paper (60°C)	68,5	± 0,6	8,02	± 0,3	6,55	± 0,3	16,0

^a Below LOQ; ^b Viscous phase sampled at 22 days**Table 3.** Elemental analysis of Oils and Viscous Phases - Halogens

in ppmw	Cl	Br
<i>Oils</i>		
Virgin PP + PE	< 30 ^a	< 30 ^a
PCW	82 ± 1,2	< 30 ^a
PCW + Paper	84 ± 1,6	< 30 ^a
<i>Viscous phase</i>		
PCW	3880 ± 196	2690 ± 6
PCW (60°C)	4740 ± 402	3400 ± 469
PCW + Paper	6050 ± 174	3070 ± 132
PCW + Paper (60°C)	5990 ± 268	3020 ± 188

^a Below LOQ; ^b Viscous phase sampled at 22 days

GCxGC

Main compounds from GCxGC analysis are highlighted in Figure 1. Typical decomposition products of PP and PE were found in all three oils. For PP these are branched olefins and alkanes, especially with carbon chain lengths that are multiples of three, e.g., 2,4-dimethyl heptane and trimethyl nonene, as well as some aromatic compounds, like toluene or xylenes. For PE mainly straight chain alkanes, 1-alkenes and α,ω -dienes are expected. In all oils the aliphatic content was dominant at 67 to 78 wt% for the PCW-derived oil, and the virgin polymer-derived oil, respectively. Aromatic species content was 9 to 11 wt%, for the PPO from virgin feedstock and PCW + Paper, respectively. In the oil derived from PCW, additionally, benzonitrile, styrene and ϵ -caprolactam were found. These are typical decomposition products of ABS or PS and PA6 respectively, indicating that the polyolefin waste contained small amounts of these polymers.

Oxygenated species, such as phenol and acetophenone were detected in the PCW and PCW + Paper oils in equal levels, not in the virgin polymer-derived one. Compounds expected from cellulose pyrolysis such as levoglucosan or furan derivatives could not be detected in any of the oils.

In the virgin polymer-derived oils no heteroatomic species could be identified.

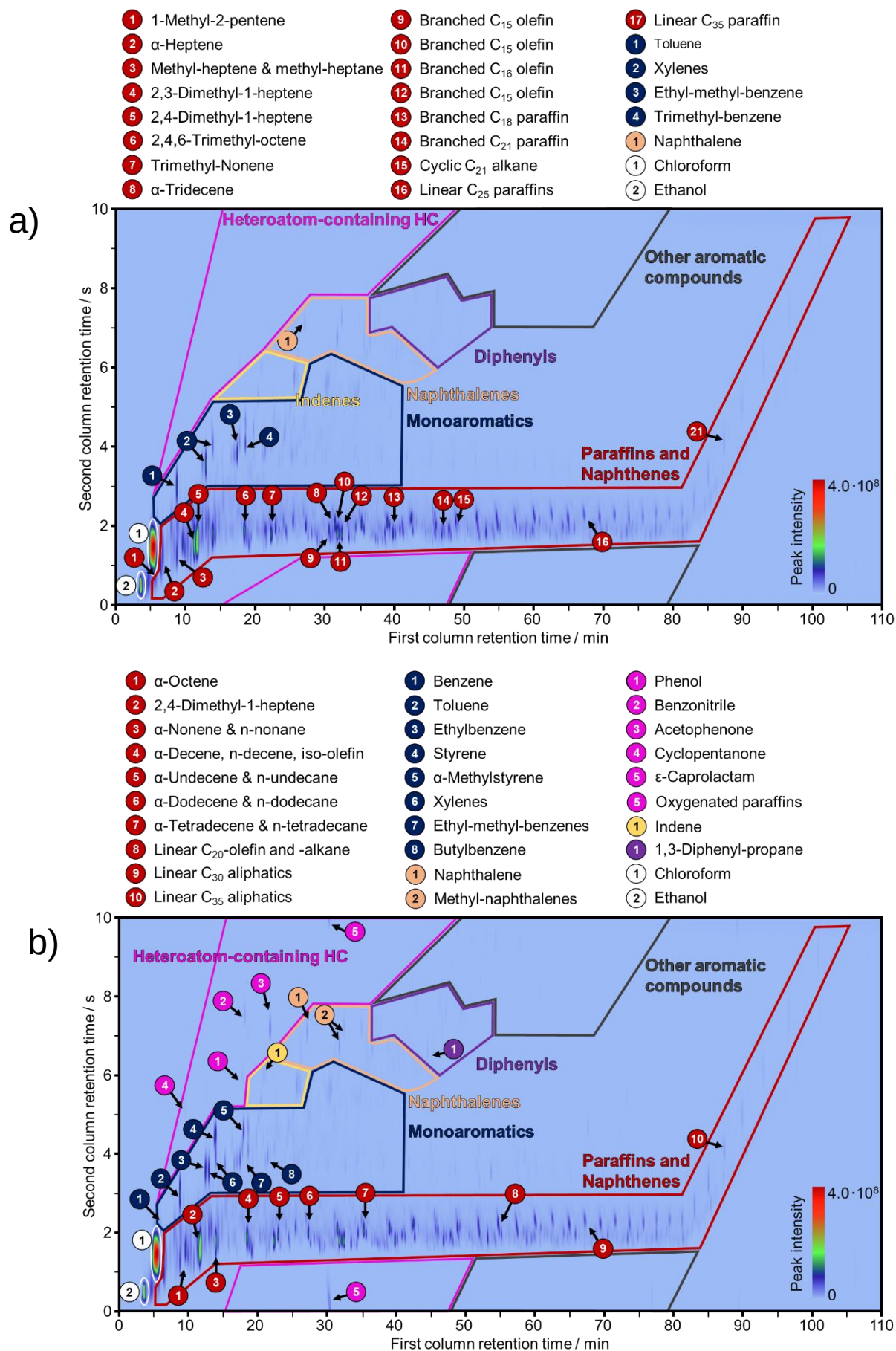


Figure 1. GCxGC chromatograms of pyrolysis oils before storage produced from (a) virgin PP and PE (70:30) and (b) post-consumer polyolefin waste.

Oil evolution

GC-FID-Screening

The chain length distributions measured by GC-FID are shown in **Figure 2**. The profiles for all three oils before storage were identical considering the measurement uncertainty. Furthermore, within the 8 weeks covered within this study, no changes in the composition were observed for any oil.

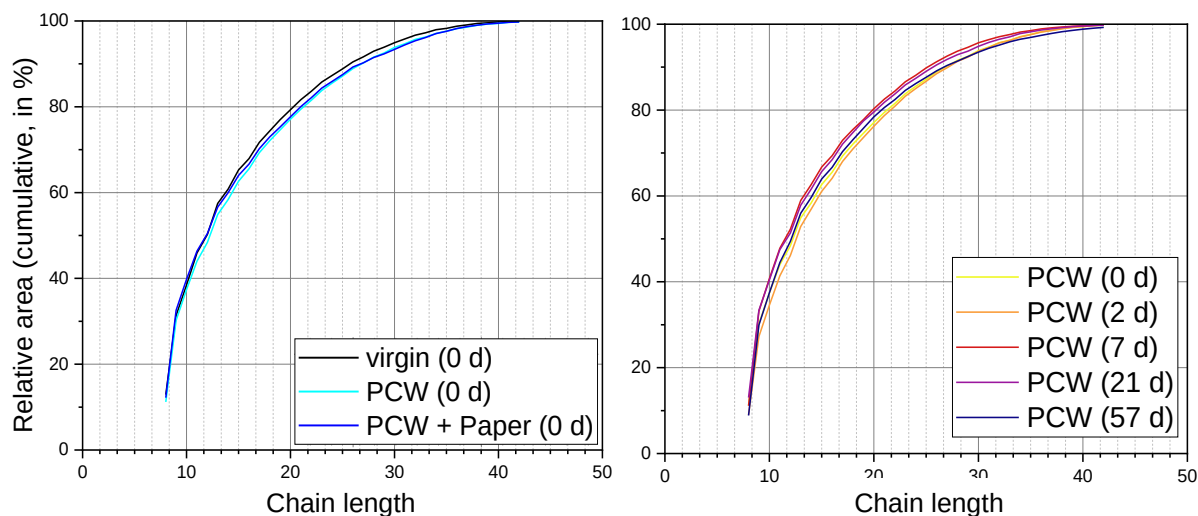


Figure 2. GC-FID cumulated relative area (in %) plotted over chain length (n-alkanes) (a) for pyrolysis oils from virgin PP and PE granulate, post-consumer waste (PCW), and post-consumer waste with 5 wt% paper added before storage as well as (b) for the PCW-derived oil stored at room temperature at all time intervals, as an example.

Viscosity

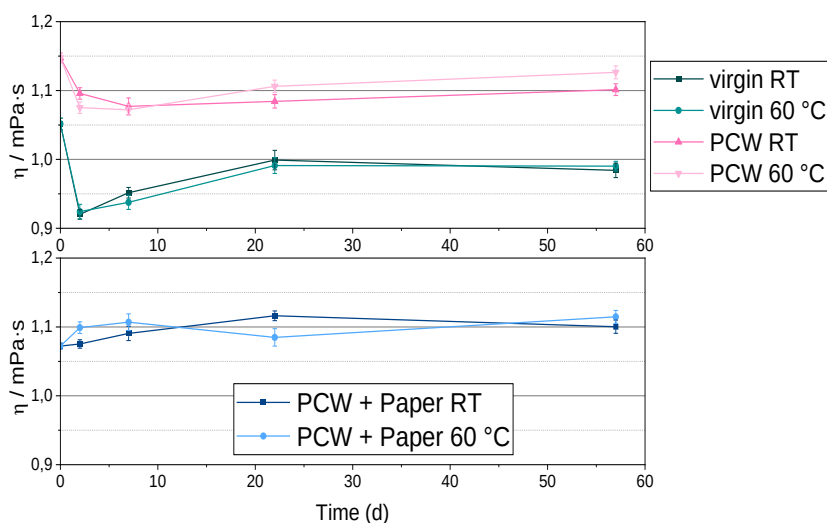


Figure 3. Dynamic viscosity at 60 °C plotted over storage time (in days) of pyrolysis oils from virgin PP and PE granulate, post-consumer waste (PCW) and post-consumer waste with 5 % paper added, each both at room temperature and 60 °C.

Viscosity measurements (Figure 3) show no clear increase over time for all three oils as had been reported by Fekhar et al. [18]. Lower viscosity values in this work are likely due to the combination of higher measuring temperature and using PP and PE rather than PE and PVC. For the PCW and the virgin material a sharp drop in viscosity within the first two days was observed for both the PPOs stored at room temperature and at 60 °C. In all cases different storage temperatures did not seem to play a role for the evolution of viscosity values.

NMR

NMR analysis of the oils shows that the oils derived from PCW and PCW + Paper contain a higher share of aromatic protons than the PPO from virgin feedstock – this corroborates the findings from GCxGC analysis. Differences between the PCW and the PCW + Paper oils are within measurement uncertainty.

For each oil, spectral regions did not experience shifts beyond measurement uncertainty over the scope of 8 weeks.

Viscous phase Formation & Analysis

On the second day after the experiment a dark brown, viscous, almost pasty phase had deposited on the wall and bottom of the flasks containing the PPO obtained from both PCW and PCW + Paper. The phase could not be dissolved by heating up to 60 °C and/or stirring the oil. An illustration is presented in **Figure 4**. It can be seen that in the flask stored at 60 °C the viscous phase is found mainly on the bottom, and much less on the walls, when compared to the flask stored at room temperature. This could indicate that, at 60 °C, the viscous phase is slowly flowing down after deposition on the walls.

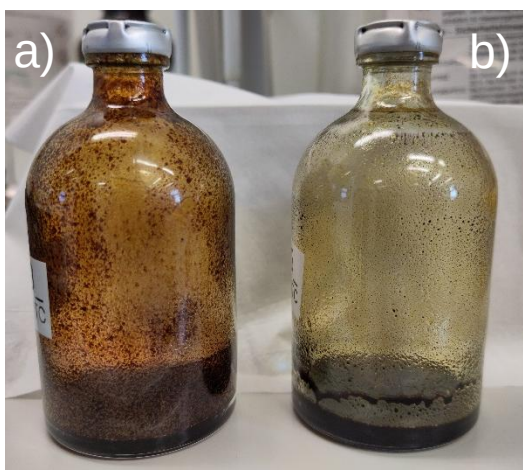


Figure 4. Photograph of viscous phase stuck to the flasks from storage of PCW + Paper-derived pyrolysis oil at (a) room temperature and (b) 60 °C after 8 weeks (57 days).

The viscous phase is partially soluble in toluene, more so in acetone, and chloroform, indicating the presence of polar compounds. Elemental analysis of the viscous phase is shown in Table 2 and Table 3. Carbon and hydrogen content dropped from 86 wt% for the oils to 66 – 72 wt%, and from around 13 to 8 – 9 wt%, respectively. H:C-ratio was also smaller than in the oils, dropping from around 1.8 to 1.38 – 1.52. Heteroatom concentrations were significantly higher in the viscous phase than in the oil. Nitrogen concentration was around 20 times higher in the viscous phase than in the oil. Chlorine concentration increased by a factor of ca. 50 or 70, respectively. Bromine concentration crossed the detection limit of 30 ppm hundredfold. The residual mass, which is ascribed to oxygen, also rose to almost 100 times its original proportion. Due to small sample amount and difficulty in extracting the sample, repeatability was generally worse, even when viewed in relation to absolute values.

Viscous phase formation could not be quantified reliably by mass balance. It can be stated that the amount of viscous phase must have been smaller than 1 % by mass relative to the sample size. Considering that the concentration of contaminants is higher by a similar magnitude, the viscous phase still could have accumulated a relevant fraction of the total heteroatom content in the oil. Repeat analysis of the elemental composition of the bulk oil over time could indicate whether this is the case.

NMR spectra of the viscous phase dissolved in deuterated chloroform generally follow the same shape as those of the oils, showing higher aliphatic proton content than aromatic. Aromatic NMR ^1H -mol% for the viscous phases increases in the order of PCW stored at 60 °C < PCW stored at RT < PCW + Paper stored at RT < PCW + Paper stored at 60 °C, *viz.* no common trend for paper addition or temperature was apparent.

Protons at chemical shift above 8.7 ppm, indicating the presence of electronegative heteroatoms species were above noise levels only for the PCW + Paper viscous phase sample from storage at 60 °C. The share of protons on aliphatic chains adjacent to heteroatom groups increased by a factor of 2.5 – 7 relative to the respective oil, in the order of PCW stored at 60 °C < PCW stored at RT < PCW + Paper stored at RT < PCW + Paper stored at 60 °C, *viz.* the same order as for aromatic protons.

The increase in heteroatom content from oil to viscous phase indicated by NMR does not relate quantitatively to the increase shown in elemental analysis. Possibly, some of the oil was physically bound in the viscous phase, giving the NMR signal, while at the same time heteroatomic compounds were present that do not contain hydrogen, or are not susceptible to ^1H NMR for other reasons. Rinsing of the flasks with a simple volatile alkane to drive out oil and subsequent drying could help confirm this idea. In addition, further analytical techniques, such as liquid chromatography or ICP-OES can provide more information on the composition of the viscous phase. Future research should look more closely at the influence of feedstock composition, rule out influence of the container material and extend the timeframe to more than 8 weeks.

Conclusion & Outlook

During the storage of post-consumer waste-derived oils, a viscous phase deposited on the bottom and walls of the container. Elemental analysis indicates that heteroatoms accumulate in this phase spontaneously.

Interestingly, the hydrocarbon composition concerning olefins was found to be the same for the virgin feedstock and the PCW, yet the viscous phase only appeared in the latter. Also, the viscous phase started to form after a day of storage, whereas storage at 60 °C for up to 8 weeks did not result in measurable changes in the hydrocarbon composition of oils, as analyzed by GC-FID and low-field NMR. This suggests that oligomerization or polymerization of olefins, which would be expected to cause a shift in chain lengths as reported in [20], was not the dominant cause for formation of the phase.

Hence, two separate mechanisms of storage instability may be acting: By the first mechanism, compounds with heteroatoms are deposited relatively quickly, and in a second slower mechanism, olefins repolymerize to form longer chains. If understood better, the former phenomenon could potentially be exploited to reduce the cost of upgrading downstream of pyrolysis, by separating a relevant fraction of the heteroatoms from the oils.

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