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Discrimination of plastic waste pyrolysis oil feedstocks using supercritical fluid chromatography

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ABSTRACT

Advanced chemical recycling techniques provide new avenues for handling and recycling mixed plastic waste; pyrolysis is a prominent approach involving heating plastic waste in an oxygen-free environment to create pyrolysis oils. Pyrolysis oils must be thoroughly characterized before being refined into fuels and chemical feedstocks. Here, a method based on supercritical fluid chromatography with ultraviolet detection was developed to analyze plastic waste pyrolysis oils. Multiple stationary phases were examined, and 2-ethyl pyridine was chosen as the best stationary phase for resolving pyrolysis oil components. Different standards and different plastic waste pyrolysis oils were compared across the different stationary phases. Up to three columns were serially coupled to increase efficiency and column capacity. It was found that a general method using ethanol as a modifier and two 2-ethyl pyridine columns could effectively resolve plastic waste pyrolysis oils. The potential for differentiating polyethylene and polypropylene feedstocks was demonstrated using principal component analysis.

1. Introduction

There is a general belief that our reliance on fossil fuels has caused an increase in global temperatures and climate change [1,2]. It is also accepted that fossil fuels are a limited resource, and eventually, the discovery of cheap and abundant petroleum will be severely reduced, causing economic strain. As such, alternative fuel sources are currently being developed [3]. A popular strategy is the pyrolysis of different materials, such as plant matter and plastic waste, to create oils, which can be further refined into fuels and chemical feedstocks [4,5]. Plastic waste pyrolysis is a form of chemical recycling where material is placed in an enclosure devoid of oxygen and then heated to decompose the substance [6]. Temperatures can range from below 400 to above 1000 °C, which chemically converts the different matter into oils comprising variable chain-length hydrocarbon species [7]. Once the oil composition is established, the resulting pyrolysis oils can be refined into useable products, such as alternative fuels or building blocks for new plastic materials.

Plastic waste pyrolysis fuels are particularly interesting due to the abundance of mixed plastic waste (MPW) feedstock available for processing [6]. The reutilization of plastic is of note due to the general concern about plastic waste pollution, which affects the environment as well as general human health [8,9]. Unfortunately, the generated plastic waste pyrolysis oils are very complex, with the number of distinct compounds estimated to be in the hundreds or thousands. The pyrolysis of MPW has been shown to generate compounds that range from fewer than six carbons to greater than forty carbons [5,10,11]. An added complexity is the variability of the MPW feedstock; the pyrolysis process produces different classes of compounds including variable heteroatom content [10,12,13]. The complete characterization of the composition of the pyrolysis oils is necessary to select appropriate subsequent refining processes. For example, many refining processes can have variable performance depending on the sulfur, oxygen, nitrogen, halogen, metal, and olefin content of the pyrolysis oil to be refined.

Generally, petroleum and other fuels are examined using gas chromatography (GC) [14–16]. As such, GC has been the primary tool

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Abbreviations: GC, gas chromatography; GCxGC, comprehensive two-dimensional gas chromatography; MPW, mixed plastic waste; SFC, supercritical fluid chromatography; CO_2, carbon dioxide; LC, liquid chromatography; PP, polypropylene; PE, polyethylene; PDA, photo diode array; BPR, backpressure regulator; 2-EP, 2-ethylpyridine; PCA, principal component analysis; UV, ultraviolet detection; HCA, hierarchical cluster analysis; FID, flame ionization detection.

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utilized when trying to identify the composition of the different types of pyrolysis oils [17]. On-line comprehensive two dimensional gas chromatography (GCxGC) is currently the most powerful single analysis technique used to discern the composition of pyrolysis oils [17,18]. The additional peak capacity provided by the second dimension aids in separating different group types from one another, in interpretable patterns. Different detectors have also been utilized, from mass spectrometry to vacuum ultraviolet spectroscopy. Each has established advantages and disadvantages. Vacuum ultraviolet spectroscopy can provide PIONA classifications and isomeric differentiation using spectral data, while mass spectrometry can provide higher sensitivity and functional group selectivity through well characterized and reproducible fragment ion spectra [16]. GC has provided some insights on mainly group-type analysis, as well as some general understanding of the effects of plastic feedstock on the composition of the plastic waste pyrolysis oil, but more work is needed. The complexity of the pyrolysis oils requires additional sample preparation or additional separations prior to the application of standard one-dimensional GC.

Supercritical fluid chromatography (SFC) is an alternative separation technique which uses high density carbon dioxide (CO_2) as the major component of the mobile phase [19–21]. SFC has been used for the analysis of petroleum products, as it is predominantly a normal phase technique [22]. SFC has a specific niche for analysis of higher molecular weight compounds that are difficult for GC to analyze, which is especially useful for plastic waste pyrolysis oils, as many higher molecular weight compounds are found. That said, very few pieces of literature examine the use of SFC for the analysis of pyrolysis oils, and most of the oils evaluated were from plant sources. SFC has been used with mass spectrometry to characterize pyrolysis oils sourced from algae [23,24]. It has been used to assist in the identification of phenols from pyrolysis oils [25]. SFC has also been used as a dimension in two dimensional separation studies aimed to characterize pyrolysis oils [26,27].

This study reports on the use of SFC with ultraviolet (UV) detection to examine plastic waste pyrolysis oils, specifically to aid in the identification of the MPW feedstock used to create pyrolysis oil. The first stage was to optimize the SFC conditions using one of the more simplistic oils as the analyte by optimizing the temperature, backpressure, flow rate, gradient, modifier, and other conditions. The method was considered optimized if it had the greatest resolution between peaks with the greatest number of peaks. The second step was to test different stationary phases to identify which phase provided the greatest resolution, as judged based on the UV chromatograms. Different pure chemical standards representing different classes of compounds were evaluated to provide greater insight into the resolution provided by different SFC column chemistries. Finally, multiple pyrolysis oils sourced from polypropylene (PP) and polyethylene (PE) were examined using the optimized methods and with each stationary phase. Created mixtures of known PP and PE content were also analyzed. This study describes an introduction for the use of SFC-UV to examine MPW pyrolysis oils. The focus was not on the molecular identification of the different components in the pyrolysis oils but rather on the generation of SFC-UV fingerprints for a cheap and easily obtainable method to differentiate oils produced from different MPW feedstocks.

2. Materials and methods

2.1. Chemical supplies and sample preparation

Instrument-grade carbon dioxide (99.99%) was purchased from AirGas (Radnor Township, Pennsylvania). The pyrolysis oils were provided by Lummus Technologies (Pasadena, Texas). Plastic waste pyrolysis oil changes composition based on the time spent in the pyrolysis tank, but due to simplicity, samples formed at the start of pyrolysis were chosen to create this introductory method. Samples could also be taken directly from the condenser line or after distillation. The plastic waste pyrolysis oil samples used in this study were taken directly from the condenser line. All standards and solvents used in this study were purchased through MilliporeSigma (Burlington, Massachusetts) or Thermo Fisher Scientific (Waltham, Massachusetts).

Asphaltenes are complex high molecular weight molecules that will precipitate in the presence of an increased n-alkane content. As heptane was used as a modifier in the SFC separations, removal of all asphaltenes was vital to prevent clogging of the chromatograph. Due to the suspected presence of asphaltenes in many plastic waste pyrolysis oils, n-hexane was added (50:50 by volume) to the oils before analysis [28]. After adding n-hexane, the sample was placed at −20 °C for one day to assist in the precipitation of the asphaltenes. The sample was then placed into a microcentrifuge for 20 min at 13,000 rpm before the supernatant was removed and placed into a 1 mL injection vial. If a sample was solid, it was heated in a water bath at 80 °C until the sample was liquid. The n-hexane was then added, the sample was centrifuged, the supernatant was removed, and the samples were stored at 30 °C, which prevented freezing of the samples.

To help provide a better understanding of the pyrolysis oils, standards were purchased based on compounds one would expect to be present in plastic waste pyrolysis oils. As alkanes and olefins do not absorb UV wavelengths, four distinct mixes were created for other compound classes. The first was an aromatic mix that contained toluene, p-xylene, 1-ethyl-4-methylbenzene, α-methyl-styrene, and 1,3-diphenylpropane. The second was a mix of nitrogen-containing compounds, which included pyrrole, quinoline, benzoquinoline, indole, and carbazole. The third mix was for oxygenates, which included benzaldehyde, phthalic acid, benzoic acid, bis-(2-hydroxyethyl) terephthalate, and phthalic anhydride. Finally, a mix that contained sulfur compounds was created using thiophene, 4,6-dimethyldibenzothiophene, and benzonaphthothiophene.

2.2. Instrumentation

SFC experiments were performed on a Nexera UC supercritical fluid chromatograph (Shimadzu Corporation, Kyoto, Japan). An LC-30ADSF pump was used to supply the liquid carbon dioxide to the system, while an LC-30AD quaternary pump delivered the solvent modifier. A SIL-30AC autosampler introduced a 2.5 µL injection of the analytes into the system with an injection loop of 20 µL. The CTO-20AC convection column oven was used to create the appropriate temperatures, with an SFC-30A backpressure regulator attached to provide the appropriate backpressure. Detection was obtained *via* an SPD-M40 photodiode array detector with a wavelength range of 190 to 400 nm. The whole system was controlled by the CBM-20A communication bus module, which was controlled through the Shimadzu Lab Solutions software.

Columns were provided generously from multiple sources. The CELERIS 2-EP, CELERIS Diol, and CELERIS Arginine columns were provided by Regis Technologies (Morton Grove, Illinois). Restek Corporation (Bellefonte, Pennsylvania) provided the Ultra Silica and Ultra Biphenyl columns. The Viridis BEH 2-PIC column was provided by Waters Corporation (Milford, Massachusetts). The ChromegaBond Silver Silica column was purchased from Perkin Elmer (Waltham, Massachusetts). Serial coupling of the columns was performed using stainless steel tubing, 1/16″ OD x 0.3 mm ID, with stainless steel nuts and ferrules purchased from Shimadzu. The tubing was cut to approximately ten cm to provide enough length for the columns to fit in the oven while maintaining minimal extra column volume.

The gas chromatograph used was a GC-2010 Plus outfitted with a flame ionization detector (FID) (Shimadzu Scientific Instruments, Columbia, Maryland). The column was an Rxi-1HT GC capillary column (Restek Corporation, Bellefonte, Pennsylvania) 30 m in length, with an inner diameter of 0.32 mm, and a film thickness of 0.1 µm. A split/splitless inlet was used and set to 325 ℃. Linear velocity was set to 47.2 cm/sec with a split ratio of 20:1 and a column flow of 3.31 mL/min. The column oven was set to hold at 35℃ for 5 min, then increased at a rate of 10 °C per minute until it reached a final temperature of 350 ℃, which

Fig. 1. A picture showing all the plastic waste pyrolysis oils tested. Note the difference in color, clarity, and viscosity. This image is to highlight the differences between plastic waste pyrolysis oils, even of the same feedstock.

was then held for 10 min. The FID was set to a temperature of 375 °C.

3. Results and discussion

3.1. Optimization strategy

The initial optimization used a plastic waste pyrolysis oil known to be a less complex pyrolysis oil with characteristics similar to natural diesel from a refinery. The oil was created from a fluid catalytic cracking pilot plant, yet had the characteristics of pyrolysis oil, including heightened olefin content at ~60 %. The oil was chosen as it could provide a comparison to existing natural fuel while also representing future pyrolysis oils to be tested. This oil was also chosen as when it was received, it was a liquid at room temperature without any apparent solids precipitating in the oil. These characteristics are not common for all plastic waste pyrolysis oils, as some oils are solid at room temperature, and some oils are turbid. This less complex oil will be termed the control oil in future references. A picture showing all plastic waste pyrolysis oils examined to highlight their visual differences, is shown in Fig. 1.

A photodiode array (PDA) detector was used, with the ability to examine 190 nm to 400 nm. Alkanes do not exhibit appreciable absorption in that wavelength range [29]. While this limits the ability of the SFC system to analyze the pyrolysis oils in total, it still provides the benefits of seeing aromatic molecules and molecules containing heteroatoms. These are especially useful as there is a gap in knowledge of compounds containing heteroatoms in plastic waste pyrolysis oils. Through experimentation, 220 nm was chosen as the primary wavelength to examine the plastic waste pyrolysis oils, with 254 nm and 280 nm being used as secondary wavelengths for examining aromatic compounds. 220 nm provided the most number of peaks without solvent suppression.

3.2. Mobile phase and stationary phase screening

Different organic solvents were tested to ensure the pyrolysis oils could dissolve readily. The organic modifiers tested were methanol, ethanol, isopropanol, acetonitrile, tetrahydrofuran, ethyl acetate, and hexane. The control pyrolysis oil was first introduced to each solvent at a 50:50 ratio in a dram vial. It was found that hexane caused precipitation, providing evidence that asphaltenes existed in the plastic waste pyrolysis oil. The oil did not fully dissolve in acetonitrile, as three distinct layers formed. All other solvents (methanol, ethanol, isopropanol, tetrahydrofuran, and ethyl acetate) could fully dissolve the control oil. The initial screening started using the Restek Ultra silica column. This column was chosen because it is an intermediatory column in polarity compared to the other SFC columns, with historical use in petroleum analysis using SFC [30,31].

Initially, an isocratic analysis was performed, starting at 15 % methanol as modifier to obtain a general idea of retention. Different gradients, as well as different starting conditions, were applied to try to find a general screening method. This general screening method was then applied to different organic solvents to understand how each modifier affected retention. The method was initially pure CO_2 held for 4 min before increasing to 20 % modifier until 14 min, followed by an increase to 40 % modifier at 19 min, which was then held until 25 min.

Ethanol was found to be the most optimal modifier as it provided the largest number of peaks while also being able to dissolve the oil. Further optimization of the gradient followed. The optimal gradient was found to be 0 % modifier for 3 min, then increasing to 40 % ethanol for 8 min before holding until 10 min. Reproducible performance of the method required that a modifier be present in the mobile phase throughout the analysis, as the presence of modifier allowed consistent pump pressure. As such, a higher initial concentration of modifier had to be used. Ethanol was tested, where the initial condition was a 5 % hold for 3 min. Ethanol was found to be too strong of a solvent, as retention of the earlier eluters disappeared entirely. Therefore, it was decided that heptane would be used at 5 % for the first three minutes as heptane is similar in solvent strength to the high-density CO_2.

The system temperature and pressure influence the mobile phase density in supercritical fluid chromatography. As the density changes, the overall retention of different compounds will also be affected. In this study, the temperatures analyzed were 30, 40, 50, and 60 °C. The pressures analyzed for the backpressure regulator (BPR) were 100, 130,

Table 1
The list of SFC parameters that were used to screen the columns.

Total Flow – 2.000 mL/min	
	Pump A – Carbon Dioxide
	Pump B – Heptane 0–3 Min; Ethanol 3–10 Min
Gradient Conditions	
	5 % [B] 0–3 Min
	5 % - 40 % [B] 3–8 Min
	40 % [B] 8–10 Min
Column Oven - 50 °C	
Backpressure Regulator	
	BPR Pressure – 150.0 bar
	BPR Temperature 50 °C
PDA: Start Wavelength 190 nm; End Wavelength 400 nm	

150, and 200 bar. It was found that the lower the backpressure, the greater the resolution in most cases, while the higher the temperature, the better the separation. Due to the limitations of certain columns, 50 °C was used for the column temperature. While the resolution was slightly better at lower backpressures, 150 bar was chosen as higher backpressure provided more consistent pumping pressures and reproducible data. All experimental conditions for the use of a single column configuration are shown in Table 1.

3.3. *Stationary phase screening*

A list of stationary phases tested is shown in Table 2. These columns were chosen due to their historical use in SFC and in petroleum analysis. Certain stationary phases were also chosen due to similarities with other stationary phases used to analyze petroleum and related products. A figure comparing each column with the control pyrolysis oil is shown in Fig. 2. The 2-ethyl pyridine (2-EP) stationary phase was selected as it provided the largest number of peaks while also having the best resolution.

3.3.1. *Serially coupling columns*

SFC enables the serial coupling of columns while reducing many of the downsides associated with coupling columns in liquid chromatography, such as a dramatic increase in pressure. After screening all the columns and choosing the 2-EP column, multiple 2-EP columns were coupled together to create more theoretical plates. Similar conditions were used, although the time interval chosen for each gradient step was doubled or tripled depending on whether two columns were coupled or three. When using three columns, the flow rate was lowered to 1.00 mL/min as the pressure increased past the column limitations. A figure comparing the use of one, two, and three 2-EP columns is shown in Fig. 3. With the addition of just one additional column, multiple peaks started to become apparent in regions where they had overlapped before. Three columns allowed almost baseline resolution of some of these peaks; more theoretical plates increased resolution.

3.3.2. *Plastic waste pyrolysis oil standards*

Mixtures of standard compounds were examined using all seven stationary phases. Each stationary phase behaved differently towards each standard mix. An example of the analysis of all the mixes using the 2-EP column is shown in Fig. 4. For the 2-EP column, which was the column decided for further plastic waste pyrolysis oil analysis, aromatic compounds tended to elute earlier, before 4 min, while compounds containing nitrogen and oxygen eluted past 7 min. Sulfur containing compounds eluted throughout the run. Certain mixes would be retained more on one column while less on another at different resolutions. Fig. 5 shows the chromatograms of the nitrogen mixture separated on each of the columns investigated in this study. The Diol column retained the mix well, but the components were hardly separated. The 2-EP column, on the other hand, retained the compounds just as well, but there was improved resolution.

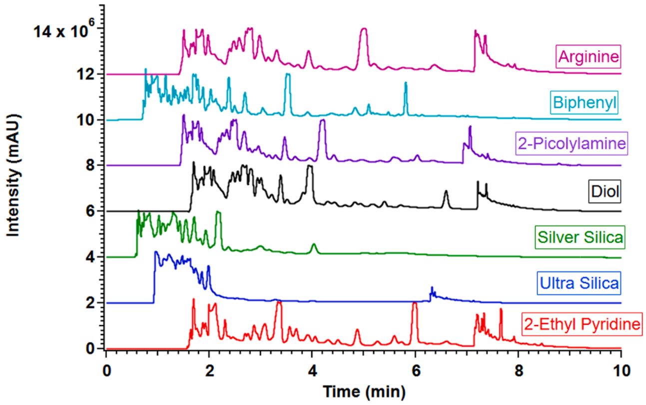

Fig. 2. A figure comparing column performance with the control pyrolysis oil. The columns tested were 2-Ethyl Pyridine (red), Ultra Silica (blue), Silver Silica (green), Diol (black), 2-Picolylamine (purple), Biphenyl (cyan) and Arginine (magenta). UV detection monitored at 220 nm.

Principal component analysis (PCA) was performed using MetaboAnalyst, a free web-based software [32]. PCA was used to visualize the variability in retention exhibited by different stationary phases. This analysis is shown in **SI Fig. 1**. It was found that the bare silica column tended to be the most different when compared to the other stationary phases, as the plot showed it is the most isolated from the other columns, indicating it exhibited greater variation from the other columns. Examination of the chromatograms shows this to be accurate, as the silica column retained the aromatic mix more readily than the other columns; this is consistent with its use in ASTM Method D6550–20 [33]. For the oxygen mixture, the silica column retained the mixture the least while all other stationary phases showed increased retention. The exception was with the nitrogen mixture, as the biphenyl column is isolated the most from the other columns in the PCA plot due to quinoline being retained longer than the method and not eluted. This shows that when performing targeted work for specific compounds and the 2-EP column is inadequate, the Ultra silica column may be a reasonable second choice.

Table 2
A list of columns and their properties that were examined in the study for SFC-UV analysis.

Column Name	Manufacturer	Stationary Phase	Column Length (mm)	Column Diameter (mm)	Particle Size (μm)
CELERIS™ 2EP	REGIS® Technologies	2-Ethyl Pyridine	250	4.6	3
CELERIS™ DIOL	REGIS® Technologies	DIOL	250	4.6	3
CELERIS™ Arginine	REGIS® Technologies	Arginine	250	4.6	5
Ultra Silica	Restek	Bare Silica	150	4.6	3
Force Biphenyl	Restek	Phenyl	150	2.1	3
Torus™ 2-PIC	Waters	2-Picolylamine	250	4.6	5
ChromegaBond Silver Silica	Perkin Elmer	Silver Silica	100	1.6	5

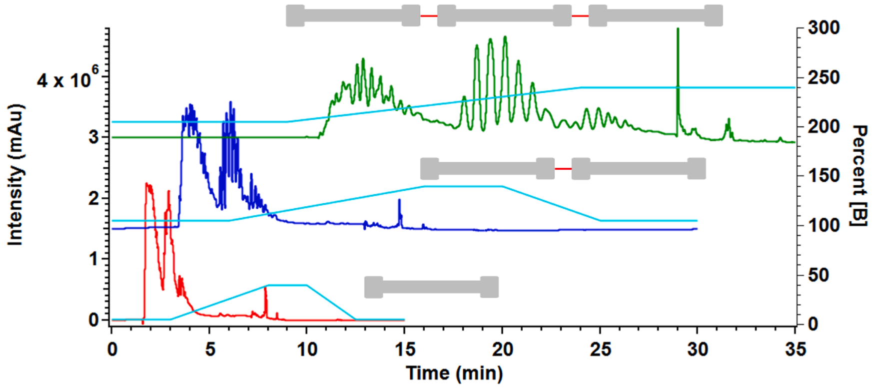

Fig. 3. Comparison of a single 2-EP column (red), two 2-EP columns (blue), and three 2-EP columns (green) for the separation of the control oil. The gradient conditions are shown with the pale blue line. UV detection monitored at 220 nm.

3.4. Plastic waste pyrolysis oil examination

After additional optimization of the method, eight additional pyrolysis oils were tested, four derived from PP feedstock and four derived from PE feedstock. It was discovered that the different plastic feedstocks provided different fingerprints in unique regions. PP oils had a larger number of compounds eluted from the 9–14 min mark, while the PE oils had a larger number of compounds eluted from the 14–19 min mark. A chromatogram showing three 2-EP columns coupled together with an example of the control oil, a PP oil, and a PE oil is shown in Fig. 6. It was later found that using two columns instead of three shortened the run by half while expressing the same regions of interest.

Further analysis was performed using PCA to understand if SFC-UV analysis was sufficient to fingerprint and differentiate feedstocks. The results of this analysis are shown in Fig. 7. The data were only examined using these fingerprint regions, and it can be seen that the different types of plastic waste feedstock cluster together, with the control oil located somewhat away from the clusters. Hierarchical Cluster Analysis (HCA) was used to examine which characteristics were similar between the plastic types, and is shown in **SI Fig. 2**. The HCA was also performed using MetaboAnalyst and shows that the SFC-UV method was able to differentiate between oil types. To further test this theory, mixtures of PP and PE oil in regular increments were created, analyzed by SFC-UV, and processed through the same PCA analysis, as seen in Fig. 8. Here, it can be shown that one can obtain a general understanding of what percentage of the oil is PP or PE based on these regions in a quick SFC run. The sensitivity also seems adequate, as there seems to be a regular progression across the PCA plot from pure polyethylene to pure

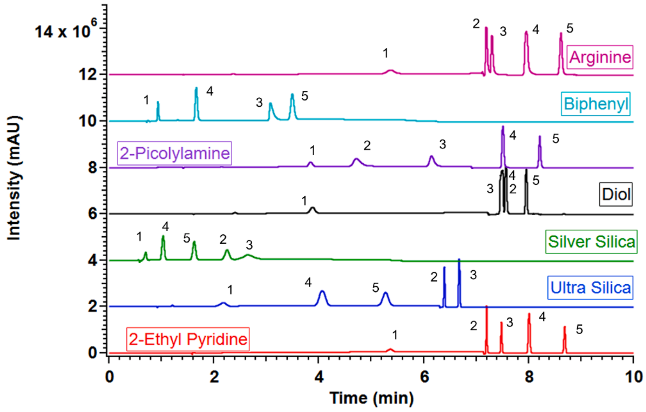

Fig. 5. Chromatograms showing the nitrogen mix on select columns. The wavelength monitored was 220 nm. The compounds were (1) pyrrole, (2) quinoline, (3) benzoquinoline, (4) indole, and (5) carbazole.

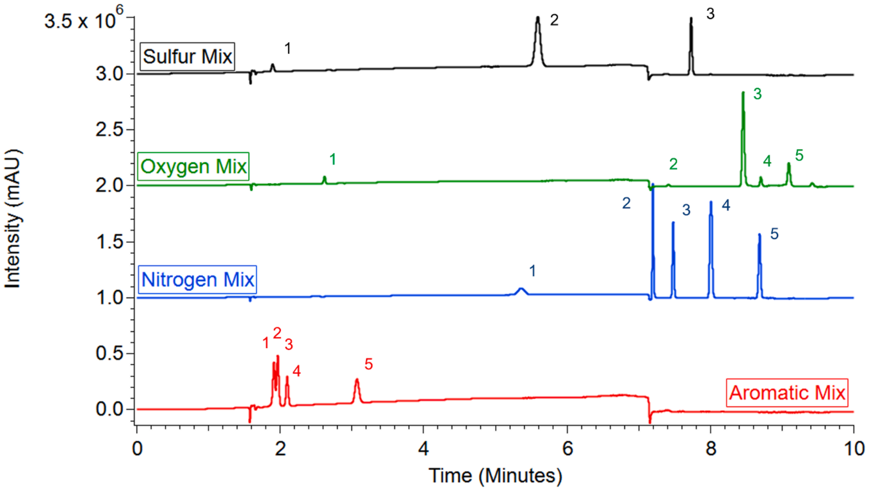

Fig. 4. Chromatograms showing the different mixes on a 2-ethylpyridine column. The wavelength monitored was 220 nm. The aromatic mixture contained (1) toluene, (2) p-xylene, (3) ethyl toluene, (4) α-methyl styrene, and (5) 1,3-diphenyl propane. The nitrogen mixture contained (1) pyrolle, (2) quinoline, (3) benzoquinoline, (4) indole, and (5) carbazole. The oxygen mixture contained (1) benzaldehyde, (2) phthalic acid, (3) benzoic acid, (4) bis-(2-hydroxyethyl) terephthalate, and (5) phthalic anhydride. The sulfur mixture contained (1) thiophene, (2) 2,6 dimethyldibenzothiophene, and (3) benzonaphthothiopene.

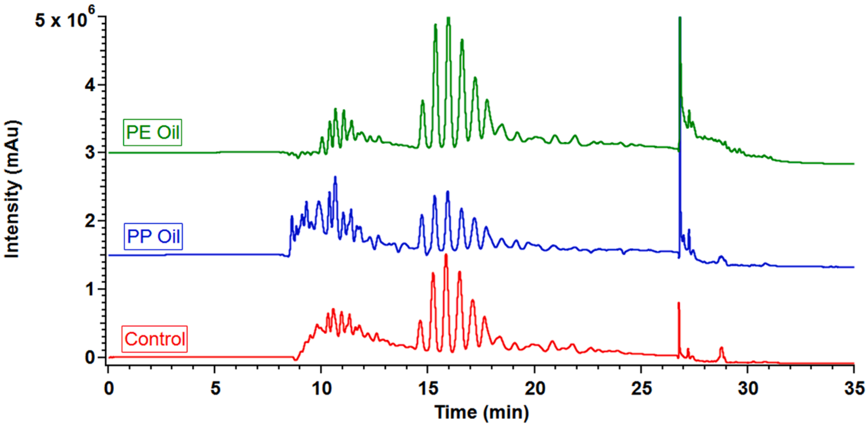

Fig. 6. Chromatograms of three different pyrolysis oils using three 2-EP columns coupled together. One is the control oil (red), one is an example of a PP oil (blue), and one is an example of a PE oil (green). UV detection monitored at 220 nm.

polypropylene pyrolysis oils.

Gas chromatography – flame ionization detection (GC-FID) is a common practice in the analysis of petroleum and other oil products. To ensure that these fingerprints were unique to SFC, all nine oils were analyzed on a GC-FID and then underwent data processing, including PCA, to try to determine if the plastic feedstock could be determined. The same three oils shown being analyzed with SFC in Fig. 6 can be seen being separated with GC-FID in **SI Fig. 3**. While the oils do look distinctly different, PCA analysis showed less correlation between the nine different oils and the plastic feedstock than when using SFC-UV. This PCA analysis is shown in **SI Fig. 4**. It is likely that signals for alkanes observed in the GC-FID analysis mask the sensitivity for discrimination of these oil types, relative to the more selective detection provided by SFC-UV, which does not detect alkanes.

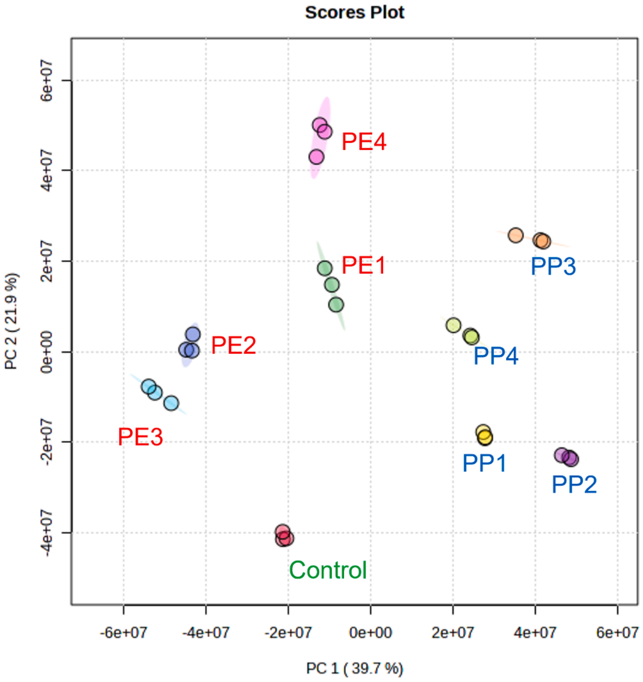

Fig. 7. A principal component analysis comparing different feedstock types and a control oil. It can be seen that the PP and the PE tend to group together on either side of the control oil.

4. Conclusion

Plastic waste pyrolysis oils are complex advanced recycling products that have been studied due to their ability to help reduce plastic waste while providing a route to circular feedstocks to reduce the need for fossil feedstocks in the industry. A method using SFC-UV was created to assist in the differentiation of oils created from different plastic waste feedstocks. Ethanol was found to be the best modifier, while 2-ethyl pyridine was found to be the best stationary phase. Nine MPW pyrolysis oils were tested: one control refined similarly to diesel, four pyrolysis oils sourced from polypropylene, and four pyrolysis oils sourced from polyethylene. Standards of known compounds that are found to be in plastic waste pyrolysis oils were also tested. These could help provide some insight regarding the elution profiles of different chemical classes on different stationary phases and provide insight into which stationary phases would be the best for targeting certain classes, since UV detection provides limited qualitative information. Finally, when undergoing PCA analysis, the SFC method could assist in determining the feedstock of the provided oil as it successfully grouped PP and PE oils distinctly. This information could also assist in the identification of which MPW produces the best oils for fuel analysis, as well as providing insight into the chemical products certain plastic types produce.

One limitation of this study is the detector chosen. Alkanes and olefins do not absorb strongly in the wavelengths typical UV detectors can examine. As pyrolysis oils are composed dominantly of alkanes and olefins, this limits the information a UV detector can provide. Nevertheless, the UV detector could distinguish fingerprint regions that assist in determining the feedstock of the MPW pyrolysis oils. Identification of the chemicals in these fingerprints could also be used in further pyrolysis oil discrimination. As the UV detector is cheaper and more available than other detectors, such as mass spectrometry, this benefits adaptation.

In the future, other plastic waste pyrolysis oils should be tested. Pyrolysis of polystyrene creates different compounds than polyethylene and polypropylene and could also provide distinct fingerprints in SFC-UV. Two-dimensional chromatography can also be utilized, as SFC provides many advantages for offline separations [34]. As certain classes of compounds elute at similar times, this method could be used for a more targeted analysis. For plastic waste pyrolysis oils to be commercially viable, MPW would be used. This creates a tremendous number of unique compounds and complicates full knowledge of the feedstock before pyrolysis. This SFC-UV method could be used to create a database of oils from well-characterized samples, which could then be used for training more sophisticated models, using for example machine learning. This approach could then help identify the plastic waste

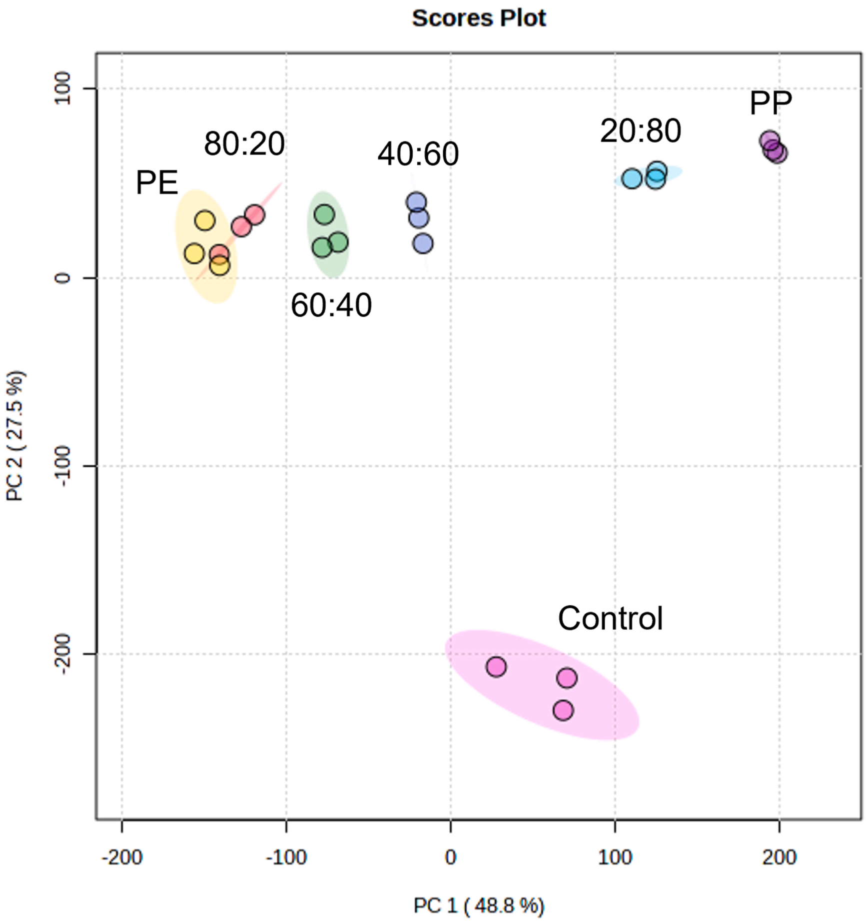

Fig. 8. A principal component analysis comparing oils formed by mixing PE and PP oils together at different concentrations. The labeled ratios are ratios of PE:PP. A linear standard progression forms between the two different oil types and their mixtures.

feedstock, and simplify the steps needed to understand the composition of the oil before further refinement.

CRediT authorship contribution statement

Alexander S. Kaplitz: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Shane Marshall:** Investigation, Formal analysis. **Niray Bhakta:** Investigation, Formal analysis, Data curation. **Sadid Morshed:** Investigation. **Jean-François Borny:** Supervision, Resources, Methodology, Conceptualization. **Kevin A. Schug:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Jean-Francois Borny reports financial support was provided by The Lummus Technology, LLC. Jean-Francois Borny reports a relationship with Lummus Technology LLC that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2024.464804.

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