



# Method development and evaluation of pyrolysis oils from mixed waste plastic by GC-VUV

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## ABSTRACT

The conversion of waste streams into a useable material through a recycling process is a hot topic. Waste streams can originate from domestic and industrial sources and range from plastic waste to medical waste to various industrial waste streams, both solid and liquid. In addition to waste circularity, circularity for bio-based waste streams and renewable sources are also being investigated. To simplify this complexity, this article presents a case study evaluating the output from the feedstock recycling of plastic waste originating from municipal solid waste.

Plastic waste entering the environment is undesired, and many initiatives are working towards a plastics circular economy. Once disposed of, ideally, plastic waste should be either re-used or recycled in order to avoid incineration or disposal in landfills. Recycling waste plastic can occur either via mechanical recycling or feedstock (chemical) recycling, where feedstock recycling can occur for example, through gasification or pyrolysis technologies. This article will focus only on the oils obtained from the pyrolysis of mixed waste plastic.

The output from pyrolysis has a different composition than traditional fossil-based hydrocarbon streams, and therefore, must be evaluated to correctly process as feedstock. The authors have previously shown that gas chromatography coupled to vacuum ultraviolet detection (GC-VUV) provides accurate identification and quantification of the hydrocarbon composition (paraffins, isoparaffins, olefins, naphthenes, and aromatics – PIONA) of fossil-based liquid hydrocarbon streams.<sup>1</sup> Therefore, GC-VUV was evaluated for analysis of the pyrolysis oils from plastic waste. Using an in-house modified spectral library in combination with the PIONA+ software, accurate identification and quantification of the hydrocarbon composition of pyrolysis oils from C<sub>4</sub> through C<sub>30+</sub> was possible with a limit of detection of 0.1 wt.%. To the best of our knowledge, this article is the first example of accurate PIONA-type quantification of pyrolysis oils by GC-VUV.

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## 1. Introduction

The conversion of waste streams into a useable material through a recycling process is a hot topic. Waste streams can originate from domestic and industrial sources and range from plastic waste to medical waste to various industrial waste streams, both solid and liquid. In addition, to waste circularity, circularity for bio-

based waste streams and renewable sources are also being investigated. To simplify this complexity, this article presents a case study evaluating the output from the feedstock recycling of plastic waste originating from municipal solid waste.

Discarded waste plastic entering the environment has been dominating headlines for the past years. Plastics can enter the environment by many means, for example, from littering to landfills. Plastic debris is a problem recognized globally, and it is still growing; even if immediately stopped, plastic debris will persist in the environment for centuries [1]. Recycling is one alternative to keeping plastic waste from entering the environment. Based on a McKinsey & Company report, of the 260 million metric tons of mixed waste plastic collected in 2016 globally, only 16% (41.6 million metric tons) was recycled [2]. Plastic recycling has two pos-

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<sup>1</sup> M.N. Dunkle, P. Pijcke, B. Winniford, G. Bellos, Quantification of the composition of liquid hydrocarbon streams: Comparing the GC-VUV to DHA and GCxGC, *Journal of Chromatography A*, 1587 (2019) 239–246. <https://doi.org/10.1016/j.chroma.2018.12.026>.

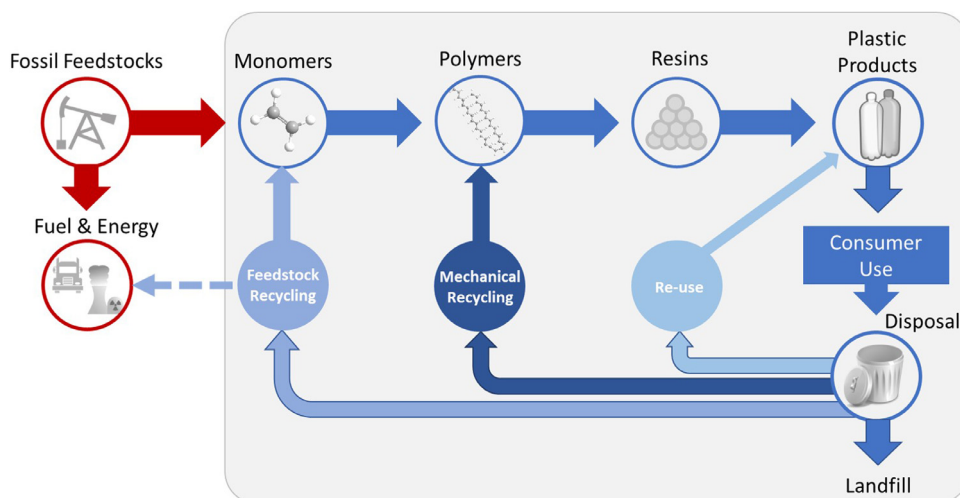


Fig. 1. Generic schematic of how mechanical and feedstock (chemical) recycling can be applied to waste plastics.

sible routes, mechanical recycling and feedstock (a.k.a. chemical) recycling. Of the two routes, mechanical recycling is already well established and practiced within existing legal frameworks. Briefly, mechanical recycling physically converts waste plastic back into a usable product by means of grinding, shredding, or melting (physical change), while feedstock recycling transforms the waste plastic through heat and/or chemical agents back into monomers (chemical change) that can be used to produce new polymers and plastic materials [3]. Fig. 1 shows a generic schematic of how mechanical and feedstock recycling can be applied to waste plastics.

Plastic materials, often called “plastics” for short, encompasses a large family of diverse materials having different characteristics, properties, and uses. There are around 20 chemically distinct classes of plastic, including polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), and polyamide (PA) to name a few. On top of that, there are many grades with different degrees of co-monomers and additives on the market; this diversity obviously creates challenges in our mission to increase recycling rates. Certain types and grades of plastic can be mechanically recycled back into new usable products once properly disposed of after use; these include PE, PP, PVC, PS, and PET. A prominent example can be found with PET bottles; while PET bottles are 100% recyclable, less than half of the produced bottles are being recycled (31% recycling rate in the US and 52% in the European Union) [4]. Brand owners are making commitments to ensure that recycled PET is included in their final products; however, one brand owner from The Netherlands, Bar-le-Duc, started offering 100% recycled plastic bottles in 2016 [5]. Mechanical recycling can handle a large range of waste plastics as a feed source, but as materials can lose quality with each recycling pass, feedstock (chemical) recycling should also be considered to ensure that all plastic waste is being recycled. With feedstock recycling, the waste plastic is (chemically) converted into a hydrocarbon stream, which can then be used to create new monomers and eventually new plastic products. Gasification and pyrolysis technologies are currently available to provide such feedstock recycling; from gasification, a synthetic gas (or syngas) is produced, while from pyrolysis, a pyrolysis oil is produced. These technologies have been recently reviewed [6–10].

For such products to be considered for use as a feedstock, a full characterization of the material is required; this article will focus on the liquid streams produced using pyrolysis technologies. Liquid hydrocarbon cracker feedstocks originating from fossil sources have a well-known hydrocarbon composition: paraffin (P), isoparaffin (I), olefin (O), naphthene (N), and aromatic (A), or

Table 1  
Platt’s hydrocarbon composition specification limits.

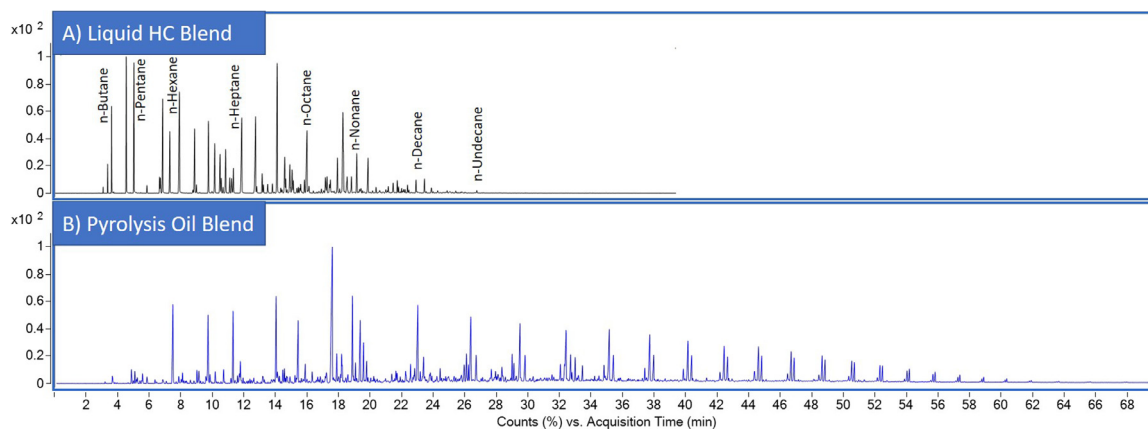
Hydrocarbon Group	Platts Spec limit (% vol.)	Converted to (% wt.)*
Paraffins	Minimum 65%	Minimum 52%
Olefins	Maximum 1%	Maximum 0.8%
Naphthenes + Aromatics	Balance	Balance

\* Representative specific gravity = 0.8 g/mL.

PIONA composition. Specifications for such feedstocks have been reported by Platts, where total paraffins ( $P + I$ ) should comprise a minimum of 65 vol.% (52 wt.%) of the material, olefins should be less than 1 vol.% (0.8 wt.%), and aromatics and naphthenes make up the balance (Table 1) [11]. However, as one can imagine, a fossil based source would have a vastly different hydrocarbon composition than one of plastic origin. For example, a polyethylene (PE) or polypropylene (PP) based plastic will have a high olefin content; a polystyrene (PS) based plastic will have a high aromatic content. In contrast, a poly(ethylene terephthalate) [PET] will have both a high olefin and aromatic content and may contain oxygenates as well. The current methodology for evaluating the hydrocarbon composition of liquid hydrocarbon feedstocks is excellent for fossil based materials [12–17]. However, they are inadequate for determining the hydrocarbon composition of pyrolysis oils originating from mixed waste plastic. If pyrolysis oils are to be considered as a potential new source of cracker feedstock, then new methodology is required to fully characterize the hydrocarbon composition of pyrolysis oils produced from mixed waste plastic.

The authors have previously shown that the hydrocarbon composition of fossil based liquid hydrocarbon feedstocks by GC-VUV is more accurate at identifying and quantifying the hydrocarbon class (PIONA) compared to the standard GC-FID method, also known as the Detailed Hydrocarbon Analysis (DHA), and both methods (GC-VUV and GC-FID) have similar repeatability [18]. The previously developed GC-VUV method was leveraged as a starting point for developing a method able to provide accurate identification and quantification of the hydrocarbon composition of pyrolysis oils originating from mixed waste plastic.

Utilization of pyrolysis oils from mixed waste plastic as a potential cracker feedstock requires full characterization of these materials. The aim of this work is to provide accurate quantification of the hydrocarbon composition by GC-VUV analysis. A detailed description of the steps and modifications taken to accomplish this are given. Additionally, a comparison of the hydrocarbon composition of fossil-based liquid hydrocarbon streams to pyrolysis oils is



**Fig. 2.** GC-VUV chromatograms (average 130 – 240 nm) obtained under the method conditions given in the Experimental above for A) liquid hydrocarbon (HC) blend and B) pyrolysis oil blend.

included to illustrate the vast differences in the hydrocarbon composition of these materials.

## 2. Materials and methods

### 2.1. Materials

Analytical standards purchased from Sigma-Aldrich (The Netherlands) were used to prepare a synthetic mixture covering a wide range of carbon number and hydrocarbon composition: Pentane, hexane, heptane, octane, decane, dodecane, 2-methylbutane, 2-methylpentane, 2-methylhexane, 1-heptene, 1-octene, cyclopentane, cyclohexane, methyl cyclohexane, ethyl cyclohexane, methyl cyclohexene, benzene, toluene, o-xylene, and isopropylbenzene. The standards were combined using equivalent volumes of each.

Several liquid hydrocarbon streams from a steam cracking plant were sourced and analyzed for the purpose of this work. Both individual liquid hydrocarbon streams and a mixture of several different liquid hydrocarbon streams were evaluated.

Several pyrolysis oils produced from the pyrolysis of mixed waste plastic were sourced and analyzed for the purpose of this work; for reasons of confidentiality, we report the sources anonymously. Both individual pyrolysis oils and a mixture of several different pyrolysis oils were evaluated.

### 2.2. Methods

An Agilent 7890B equipped with an Agilent 7693A autosampler was coupled to the VGA-100 from VUV Analytics Inc. (Da Vinci Laboratory Solutions, Rotterdam, The Netherlands). Instrument control and data processing were performed using OpenLab (C.01.07SR3), VUVision (V 2.9.4) and the PIONA+ (V 1.1.1) software package. The column utilized was an HP-PONA (50 m x 0.200 mm x 0.50  $\mu\text{m}$ ) purchased from Agilent Technologies, Middelburg, The Netherlands). An injection volume of 0.2  $\mu\text{L}$  was utilized with the Split/Splitless injector set to 275  $^{\circ}\text{C}$  and a split ratio of 50:1. Helium was used as the carrier gas at a constant flow of 1.5 mL/min. The transfer line and flow cell temperatures were set to 275  $^{\circ}\text{C}$ , and the make-up gas was nitrogen at a constant pressure of 0.25 psi. The oven program was 30  $^{\circ}\text{C}$  (4 min) – 5  $^{\circ}\text{C}/\text{min}$  – 310  $^{\circ}\text{C}$  (10 min), which corresponds to a 70 min run time.

For data processing, the background was taken from 1.4 – 1.6 min, and the chromatograms were analyzed from 2 – 69 min in steps of 0.2 min. The chromatogram filters were set to 125 – 240 nm (8071), and a spectral library, modified in-house with various olefin spectra ranging in carbon number from  $\text{C}_5$  –  $\text{C}_{30}$ , was utilized for identification and quantification purposes.

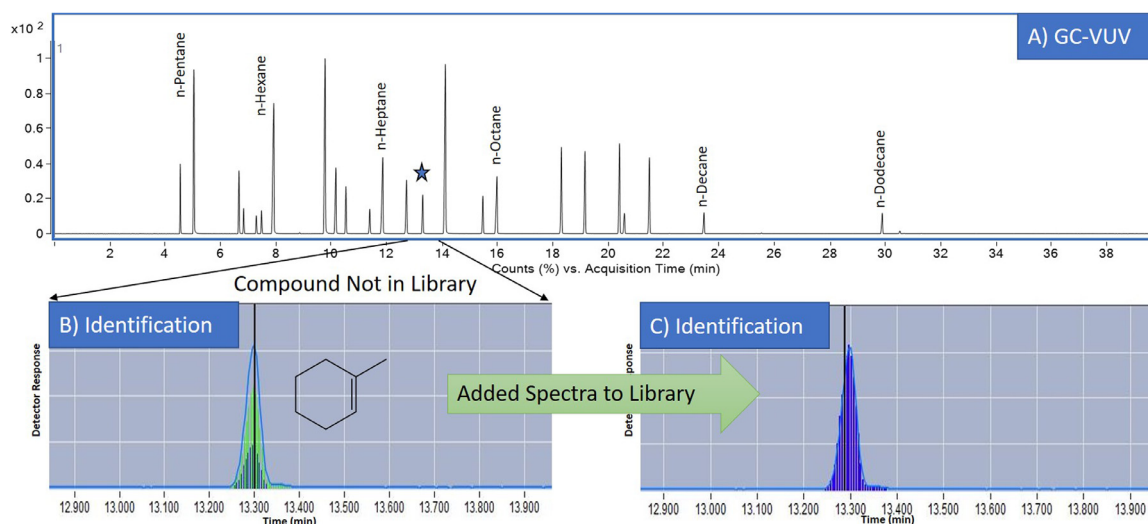
## 3. Results and discussion

### 3.1. Obtaining accurate PIONA quantification

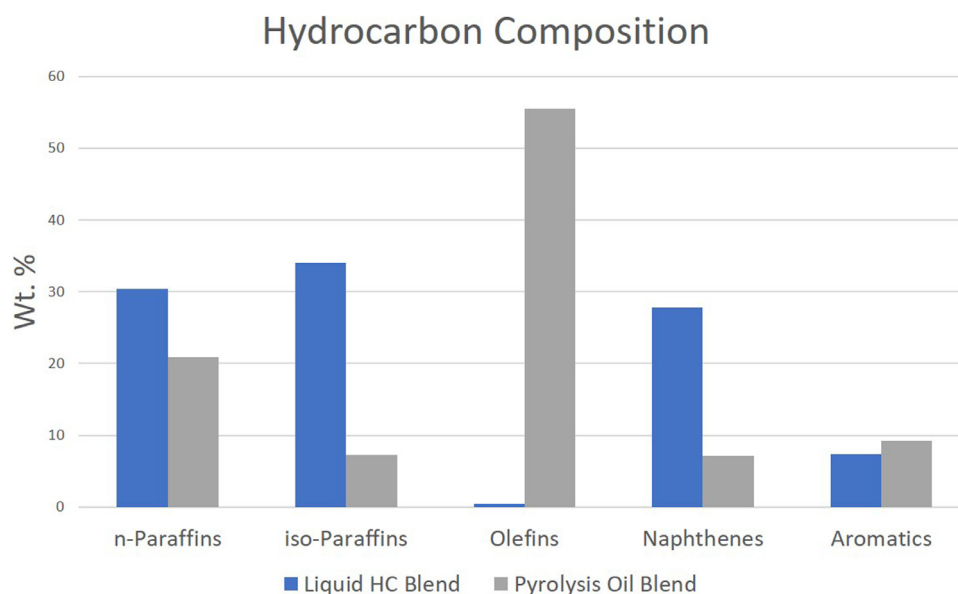
A GC-VUV method previously developed for quantification of the hydrocarbon composition of liquid hydrocarbon streams [18] was extended to afford the elution of higher molecular weight compounds. Fig. 2 shows the GC-VUV separation for both a liquid hydrocarbon blend and a pyrolysis oil blend. It is clear to see the difference in profiles and carbon number ranges between the two samples, where the liquid hydrocarbon blend ranged from  $\text{C}_4$  –  $\text{C}_{11}$  and the pyrolysis oil blend ranged from  $\text{C}_4$  –  $\text{C}_{32}$ .

Peak identification and quantification of the GC-VUV chromatograms was performed using a previously described time interval deconvolution method [19–21]. This method considers the UV spectra and corresponding relative response factors incorporated into the spectral library. In order to accurately identify the hydrocarbon composition of the pyrolysis oil blend, a multitude of VUV spectra, together with calculated response factors, were added to the spectral library. An example of the importance of including additional spectra is given in Fig. 3. A synthetic sample was prepared using analytical standards and was analyzed by GC-VUV. It was observed that the peak corresponding to methyl cyclohexene was split into two different compound classes as shown by the dark and light portions of the peak in Fig. 3B. Upon further investigation, this compound's spectrum was not present in the VUV spectral library, which explains why the peak was deconvoluted into an olefin and a naphthene. The collected spectrum for this compound was then added to the spectral library, which upon re-analysis of the data file yielded a single identified compound peak.

Another point for consideration when modifying the VUV spectral library is the relative response factor (RRF) for the compound(s) being added. Care must be taken with the inclusion of accurate RRFs, as it has been reported that different compounds have different VUV responses; for example, aromatics have the highest VUV sensitivity compared to the other compound classes owing to the presence of  $\pi$ -electrons, which can undergo high probability transitions [22,23]. Therefore, when including new spectra into the spectral library, accurate RRFs must accompany the entry, or quantification of the hydrocarbon composition will be erroneous. For a detailed description on how the RRF from GC-VUV data was determined, the readers are referred to [19]. Briefly, the RRFs were determined relative to methane, which was assigned an RRF value of 1. Once an RRF for a compound is assigned



**Fig. 3.** A). GC-VUV chromatogram (average 130 – 240 nm) of a synthetic mixture with n-paraffin peaks annotated, B) deconvolution and identification prior to adding the compound spectrum to the spectral library, and C) deconvolution and identification after adding the compound spectrum to the spectral library.



**Fig. 4.** PIONA quantification of the liquid hydrocarbon (HC) blend and pyrolysis oils blend from the GC-VUV data shown in Fig. 2.

( $RRF_1$ ), the RRF for any other compound ( $RRF_2$ ) can be determined using:

$$\frac{RRF_2}{RRF_1} = \frac{M_2 A_1}{M_1 A_2} \quad (1)$$

where  $M_2/M_1$  is the relative mass of the two analytes and  $A_1/A_2$  is the ratio of measured response areas of the two components. Example RRF values for selected compounds are given in Table 2.

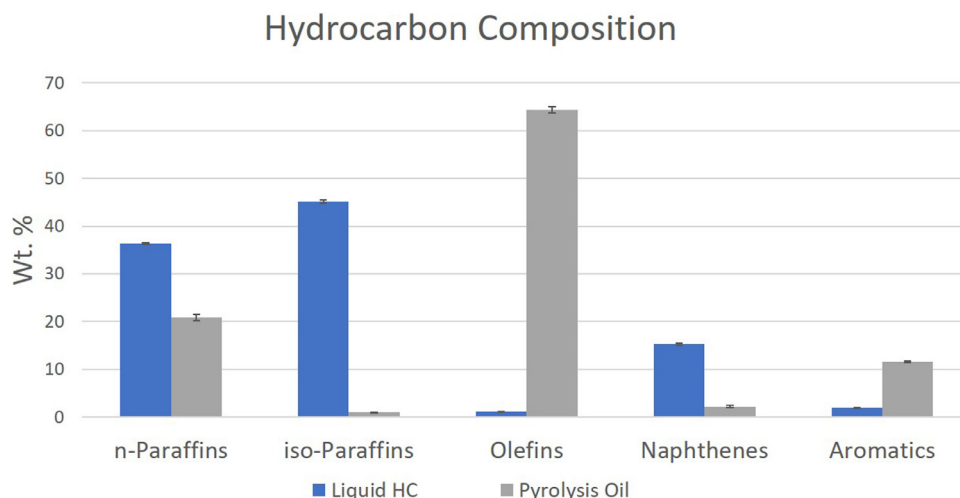
Using the in-house modified VUV spectral library and the PIONA+ deconvolution program, the hydrocarbon composition was quantified for the liquid hydrocarbon blend and the pyrolysis oil blend. Fig. 4 contains the bar plots for the n-paraffin, isoparaffin, olefin, naphthene, and aromatic, also known as PIONA, quantification across the observed carbon range for the two samples. As can be seen, the hydrocarbon composition between a fossil-based feed and pyrolysis oils originating from mixed waste plastic are vastly different.

**Table 2**  
Example VUV RRFs for select compounds relative to methane (RRF = 1.0).

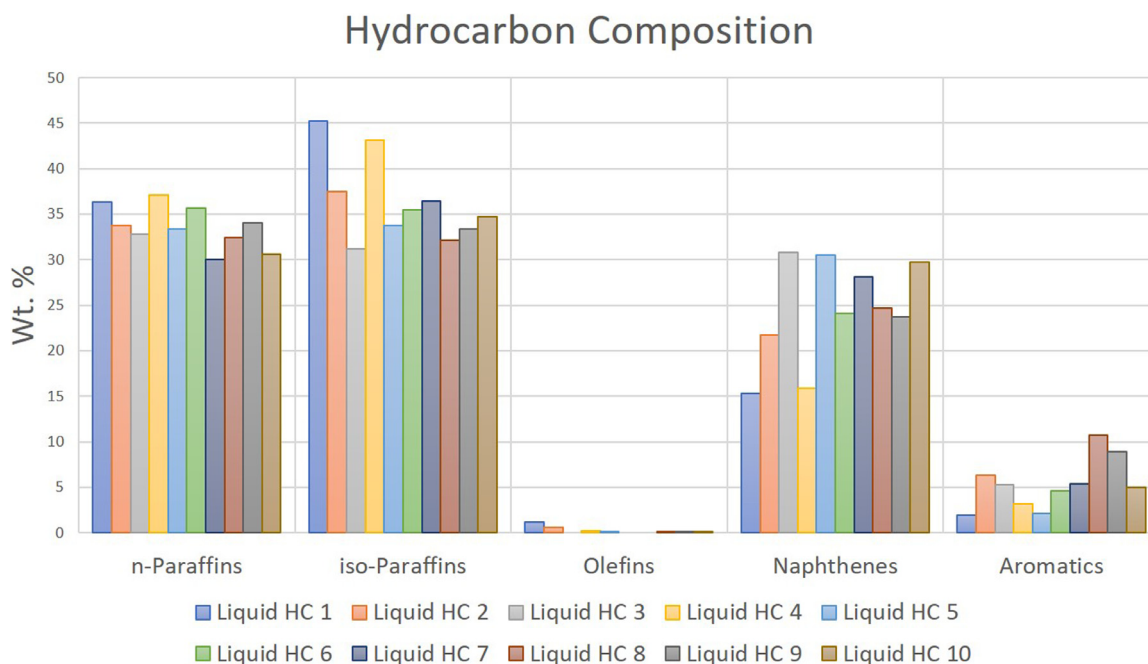
Compound	PIONA Classification	VUV RRF
Hexane	Paraffin	0.769
Heptane	Paraffin	0.769
2-methylpentane	Isoparaffin	0.781
2-methylhexane	Isoparaffin	0.781
1-Hexene	Olefin	0.465
1-Octene	Olefin	0.465
Cyclohexane	Naphthene	0.786
Methylcyclohexane	Naphthene	0.786
Benzene	Aromatic	0.285
Toluene	Aromatic	0.267

### 3.2. Method repeatability

As the hydrocarbon composition of the liquid hydrocarbon blend and pyrolysis oil blend shown in Fig. 4 differ extremely from one another, the method repeatability was assessed for both sam-



**Fig. 5.** PIONA quantification of the 2-day repeatability study for liquid hydrocarbon stream 1 and pyrolysis oil 1 ( $n = 10$  injections/day). Error bars show the spread over the two days; for concentrations above 3 wt.%, RSDs were less than 3.3%, and for concentrations less than 3 wt.%, RSDs were less than 10%.



**Fig. 6.** PIONA quantification from the GC-VUV analysis of 10 different liquid hydrocarbon samples.

ple types. A 2-day repeatability study was performed using one of the sourced liquid hydrocarbon streams and one of the sourced pyrolysis oils. Each sample was injected  $n = 10$  times a day on each of the two days. Fig. 5 shows the PIONA quantification for the two samples, including error bars representing the standard deviation of the combined 20 injections over the two days. The largest deviations were found for PIONA values less than 3 wt.% in the samples. For concentrations above 3 wt.% in the samples, all relative standard deviations (RSDs) for PIONA quantification were less than 3.3%, and for concentrations less than 3 wt.% in the samples, all RSD values for PIONA quantification were less than 10% RSD. An explanation for the larger deviation observed for the PIONA quantification at lower concentration levels ( $< 3$  wt.%) is because the individual PIONA contribution per carbon number is close to the limit of quantification (LOQ) of the method across a range of carbon numbers, which upon summing all of the PIONA contributions per carbon number, results in an increase in the deviation compared to PIONA contributions per carbon number that are well

above the LOQ. Even still, these results show that the method is repeatable for both sample types and across a wide range in hydrocarbon composition.

To determine the limit of detection (LOD) and limit of quantification (LOQ) for the method, individual compounds were assessed, rather than the summed PIONA values. The LOD and LOQ were determined using the standard deviation ( $S$ ) of a low concentration of 1-octene spiked in a liquid hydrocarbon stream ( $n = 10$  injection), where the  $LOD = 3 \times S$  and  $LOQ = 10 \times S$ . The LOD was determined to be 0.1 wt.%, and the LOQ was determined to be 0.3 wt.%. It should be noted that the determined LOD and LOQ for individual compounds are in line with the current GC-VUV method used for PIONA quantification of fuels [17].

### 3.3. Evaluation of pyrolysis oils

The method can accurately and precisely identify and quantify the PIONA composition of not only liquid hydrocarbon streams,

## Hydrocarbon Composition

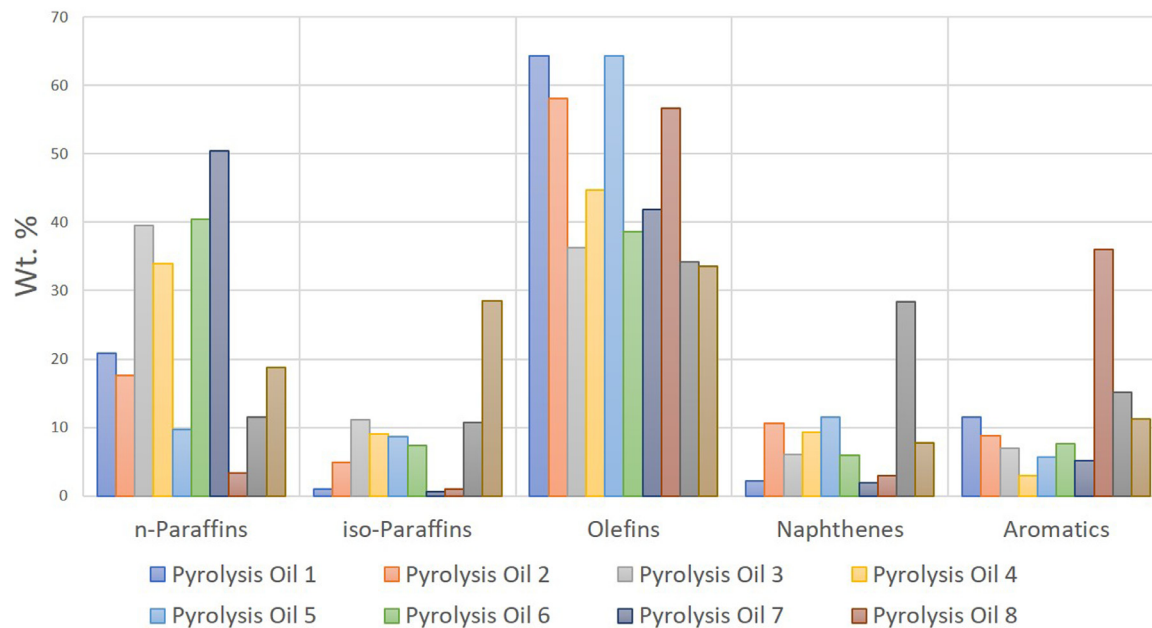


Fig. 7. PIONA quantification based on the GC-VUV analysis of 10 different pyrolysis oils from mixed waste plastic.

but also pyrolysis oils originating from plastic waste. Several liquid hydrocarbon streams and pyrolysis oils were sourced to evaluate against the developed GC-VUV method. Figs. 6 and 7 show the PIONA composition obtained for 10 different liquid hydrocarbon samples and ten different pyrolysis oils originating from plastic waste, respectively.

Upon evaluation of the ten different liquid hydrocarbons samples by GC-VUV, it was clear to see that the overall PIONA compositions were quite similar. In terms of meeting industry standards, for which the Platt's specifications are typically utilized (see Table 1) [11], the combined paraffins (P) and isoparaffins (I) is above 52 wt.% of the sample, and olefins (O) are less than 0.8 wt.% for all of the liquid hydrocarbon streams evaluated (Fig. 6). Variation in the naphthenes (N) and aromatics (A) is observed; however, these classes only need to be reported, so variation is allowed.

Evaluation of the ten different pyrolysis oils originating from mixed waste plastic by GC-VUV yielded a very different picture compared to the liquid hydrocarbon streams. The PIONA quantification for the 10 pyrolysis oils is given in Fig. 7. As expected from the initial results presented above, none of these samples meet the Platt's specifications; the combination of the paraffins (P) and isoparaffins (I) does not meet 52 wt.%, and the olefins (O) are well above 0.8 wt.% in all of the samples analyzed. The obtained hydrocarbon composition is also entirely expected, as it is well known that upon pyrolysis, PE will form a series of alpha-omega diolefins with the corresponding mono-olefin and n-alkane [24]. The variation within the PIONA classes is extremely high, averaging around 30 wt.% difference between samples. This variation is likely due to the wide array of plastics comprising the plastic waste. For the purpose of this work, the type of plastic waste used to prepare the pyrolysis oils was generalized as mixed waste plastic, specific details on the breakdown of the composition are unknown.

#### 4. Conclusions

This article expands the capability of GC-VUV to include the PIONA quantification of pyrolysis oils. The previously developed GC-VUV method for liquid hydrocarbon streams was leveraged and

expanded specifically for the analysis of pyrolysis oils originating from mixed waste plastic. As pyrolysis oils have a different hydrocarbon composition compared to fossil-based feedstocks, the VUV spectral library was enhanced with a multitude of spectra representative of components in pyrolysis oils, taking care to include accurate relative response factors. By enhancing the spectral library, the power of the GC-VUV PIONA+ deconvolution software was fully exploited, providing accurate identification and quantification of the hydrocarbon composition of the studied pyrolysis oils.

To the best of our knowledge, for the first time, the hydrocarbon composition of pyrolysis oils from mixed waste plastics was accurately characterized using GC-VUV. The method showed good repeatability and was applicable to both fossil-based hydrocarbon streams and pyrolysis oils, which have vastly different hydrocarbon compositions to one another. While only a first step, these data show progress towards the complete characterization of pyrolysis oils originating from mixed waste plastic, which is necessary if a plastics circular economy is to be realized.

This work establishes a better understanding of the hydrocarbon composition of pyrolysis oils generated from mixed waste plastic. It has been shown that these materials are vastly different in hydrocarbon composition (PIONA) compared to fossil-based liquid hydrocarbon streams, which will need to be addressed if such materials are to be utilized in feedstock recycling. To fully exploit feedstock recycling, the hydrocarbon composition of pyrolysis oils originating from other waste streams must also be evaluated. While not presented in this article, the developed GC-VUV has been leveraged to the pyrolysis oils from other waste materials as well as bio-based and renewable sources, which is currently work in progress.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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

### CRedit authorship contribution statement

**Melissa N. Dunkle:** Conceptualization, Methodology, Validation, Writing - original draft, Writing - review & editing. **Pascal Pijcke:** Conceptualization, Formal analysis. **William L. Winniford:** Conceptualization, Supervision. **Matthijs Ruitenbeek:** Resources. **George Bellos:** Resources.

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