



APPLICATION HIGHLIGHT:

PIONA Group-Type Analysis of PE and PP Pyrolysis Oils by GCxGC-FID



Introduction:

Plastic waste is one of the major environmental problems in the world. Therefore, increased investments are made in the chemical recycling of plastics. After collection and sorting, the first process into recycling plastics is to convert the raw plastics into a liquid form which is easier to process. This is usually done using pyrolysis reaction processes to create a pyrolysis oil, which some may refer to as liquified plastics.

These pyrolysis oils can either be used as a co-blended feed for normal refinery processes, such as FCC, or processed via steam crackers back into the core feed stocks to produce plastics, like ethylene and propylene. Determining the composition of this pyrolysis oil is therefore of crucial importance to optimize the process control of the pyrolysis reaction itself and to know the composition before being used as a feed in subsequent processes.



Pyrolysis oils are complex mixtures containing paraffins, naphthalene's, aromatics and olefins varying in concentration for each group and vary in boiling range distribution. The AC custom group type analysis of pyrolysis oils from waste polyethylene and propylene can provide the desired separation power to determine the pyrolysis oil composition.

PAC's Customized Application on Compositional Analysis of WPPO:

As part of its extensive portfolio of GC based analyzers for the HPI industry, PAC is offering a custom GCxGC-FID solution capable to give a group type separation for middle distillate products up to 450°C. (i.e. hydrocarbon chain length of n-C30).

This GCxGC-FID solution is based on a "reversed phase and reversed flow" configuration. A polar column is used as first dimension, and a non-polar for the second dimension. The advantage of this setup is that the separation between each group is much clearer than in normal phase GCxGC-FID, which allows a much better group-type identification and thus quantification of paraffins, naphthalene's and aromatics. The "reversed flow" refers to flow modulation with a high flow in the reversed direction to empty the loop on the second-dimension column. To simplify the use and quantification detection is done by FID, a common used and robust detector having a long dynamic measurement range.

PAC started with the development of a GCxGC-FID application focused on jet fuels and diesels. However, the group type separation it provides in separating the n-paraffins, iso-paraffins, naphthalene's, aromatics and individual components can be applied to any HPI or petrochemical product that falls in the boiling range of the application. Therefore, the GC application can also be used for the composition analysis of pyrolysis oils made from waste plastics, like from polyethylene and polypropylene, as long as the pyrolysis oils do not extend over the maximum boiling range of 450°C.

The 2D-plots in Figures 1 and 2 below clearly demonstrate the separation and identification of AC's customized GC solution for diesel fuel containing FAME's and of a pyrolysis oil from polyethylene.

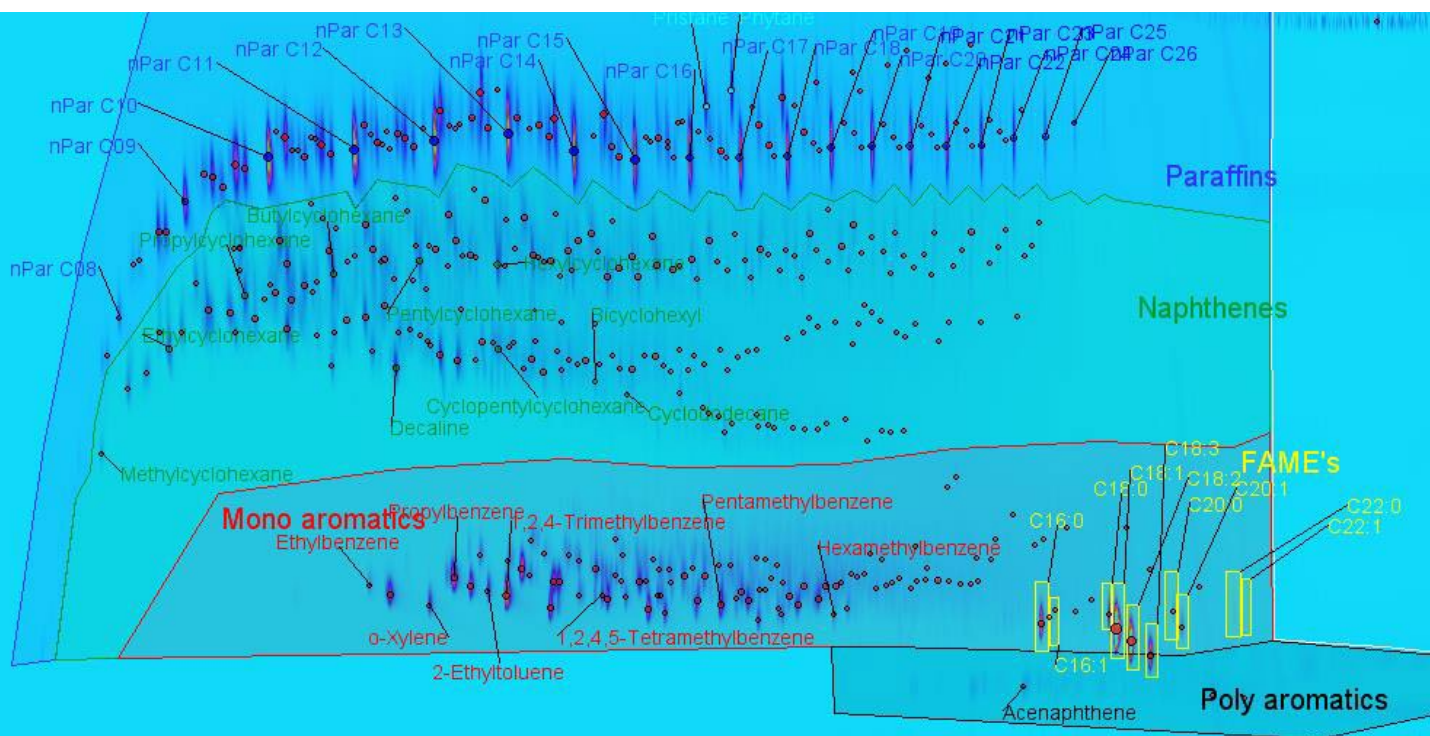


Figure 1: GCxGC 2D-plot of a diesel fuel containing FAME's.



Figure 3 shows a 2D-plot of a pyrolysis oil from PE where clearly the band of α -olefins can be identified and quantified. The pyrolysis of PE also produces n-paraffins, which can also be identified and quantified.

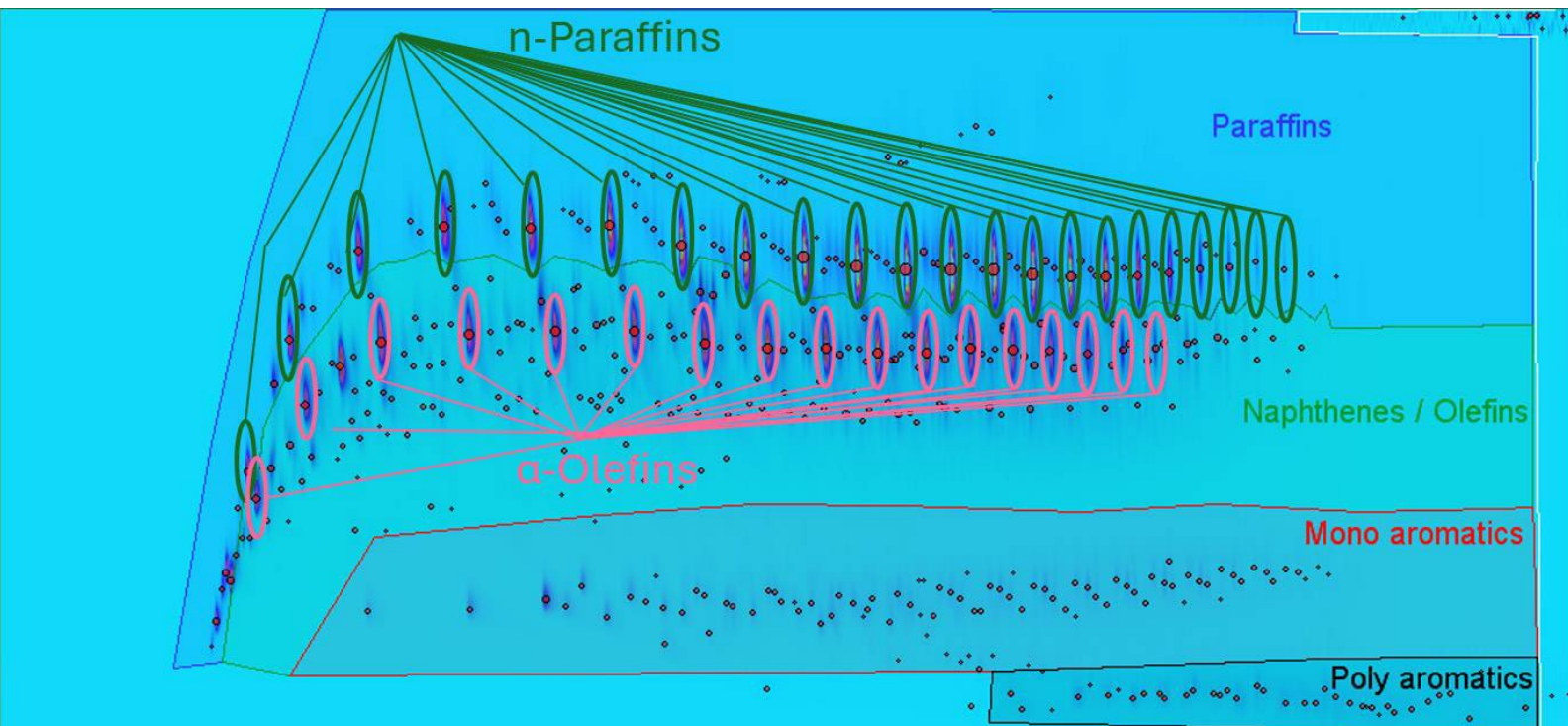


Figure 3: GCxGC 2D-plot of a PE-rich pyrolysis oil containing high amount of n-paraffins & α -olefins.

The pyrolysis oil of polypropylene results in a more complex mixture, where specific groups of olefins and iso-paraffins can be distinguished and reported, as can be seen in Figure 4.

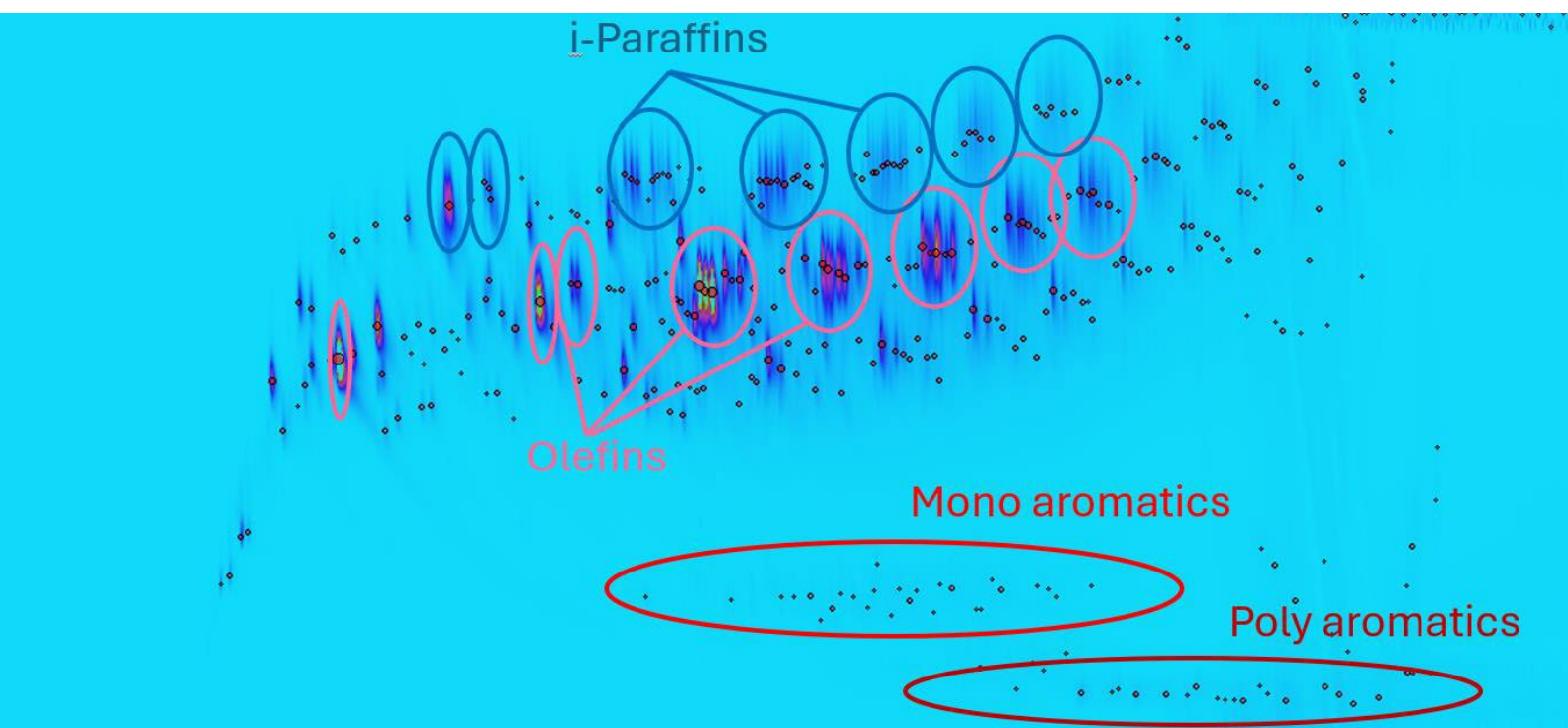


Figure 4: GCxGC 2D-plot of a PP-rich pyrolysis oil.



How Can this Custom GC Solution Work for You?

The strength of the GC application is that it gives clear group-type separation and in the case of pyrolysis oils of PE and PP the olefins can be distinguished and identified from the co-eluting naphthene group. This allows the application to be successfully used to report the PIONA composition for these pyrolysis oils.

Quantification is done using theoretical response factors for FID detectors using below formula. This formula is already successfully used in standardized methods like ASTM D6839, ASTM D6730 and ASTM D8396. The groups and individual components are calculated using these theoretical response factors and normalized to 100% to give the full PIONA composition in mass%.

$$RRF = \frac{[(C_{aw} * C_n) + (H_{aw} * H_n)] * 0.7487}{(C_{aw} * C_n)}$$

Where:

- RRF = relative factor for a hydrocarbon type group of a particular carbon number,
- C_{aw} = atomic mass of carbon b 12.001,
- C_n = number of carbon atoms in the hydrocarbon type group, of a particular carbon number,
- H_{aw} = atomic mass of hydrogen b 1.008,
- H_n = number of hydrogen atoms in the hydrocarbon type group of a particular carbon number, and
- 0.7487 = factor to normalize the result to a methane response of unity, (1).

PAC has already successfully delivered this application for the PIONA analysis of pyrolysis oils of PE and PP where the end user has further optimized the identification template to their process. PAC delivers the application with a standard identification template for quantifying the main groups; paraffins, n-paraffins, naphthene's/olefins, and aromatics.

The GC-image software provided with the GCxGC-FID application allows the end-user to further optimize the standard identification template PAC supplies to suit their process. A simple example of a further optimized identification template for a pyrolysis oil from polyethylene can be seen in Figure 5 and the reported values in Table 1. In this example, the α -olefins are individually identified and summed to report a total α -olefins. The identification template can be customized much further and tailored to the end-user preference.



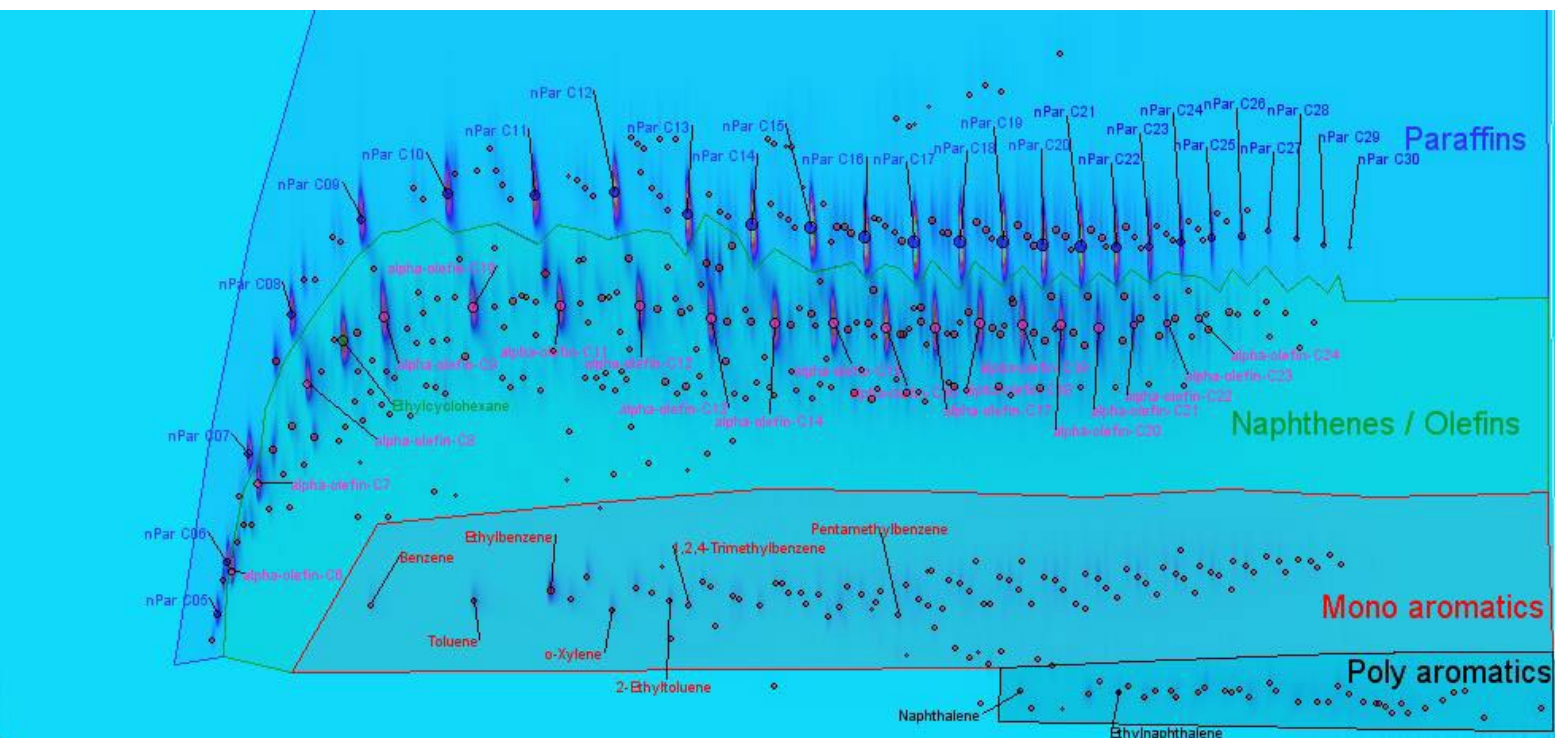


Figure 5: GCxGC 2D-plot of a PE-rich pyrolysis oil with the individual α -olefins identified.

Blob ID	Compound	Group	Inclusion	Internal Std.	Retention I (min)	Retention II (sec)	Peak Value	Volume	Amount %
32	alpha-olefin-C6	alpha-olefins	true	0	8.52	0.77	77	2807	0.47
31	alpha-olefin-C7	alpha-olefins	true	0	9.51	1.16	77	3848	0.65
30	alpha-olefin-C8	alpha-olefins	true	0	11.32	1.61	78	6336	1.07
26	alpha-olefin-C9	alpha-olefins	true	0	14.12	1.91	89	8998	1.52
29	alpha-olefin-C10	alpha-olefins	true	0	17.38	1.95	84	7879	1.33
25	alpha-olefin-C11	alpha-olefins	true	0	20.59	1.96	88	8842	1.49
23	alpha-olefin-C12	alpha-olefins	true	0	23.51	1.96	96	9819	1.65
20	alpha-olefin-C13	alpha-olefins	true	0	26.13	1.90	101	9639	1.62
14	alpha-olefin-C14	alpha-olefins	true	0	28.47	1.88	125	9942	1.67
15	alpha-olefin-C15	alpha-olefins	true	0	30.62	1.88	120	9831	1.66
13	alpha-olefin-C16	alpha-olefins	true	0	32.55	1.86	135	9340	1.57
16	alpha-olefin-C17	alpha-olefins	true	0	34.36	1.86	121	9511	1.60
18	alpha-olefin-C18	alpha-olefins	true	0	35.99	1.88	115	9839	1.66
27	alpha-olefin-C19	alpha-olefins	true	0	37.57	1.87	89	81.58	1.37
33	alpha-olefin-C20	alpha-olefins	true	0	38.97	1.87	66	6968	1.17
37	alpha-olefin-C21	alpha-olefins	true	0	40.37	1.86	48	6994	1.18
46	alpha-olefin-C23	alpha-olefins	true	0	42.87	1.88	22	1693	0.29
91	alpha-olefin-C24	alpha-olefins	true	0	44.04	1.90	12	1604	0.27

Area ID	Area	Group	Internal Std.	Retention I (min)	Retention II (sec)	Peak Value	Volume	Amount %
32	Mono-aromatics		0	20.24	0.68	26	38004	6.83
31	Naphthenes & Olefins		0	32.55	1.86	135	287964	47.89
33	Paraffins		0	36.87	2.25	285	230059	43.34
34	Poly-aromatics		0	44.27	0.25	6	11484	1.94

Name	Type	Included Volume (total)	Included Percent Response (total)	Amount Percent (total)	Amount Source
n-Paraffins	Group	185452	33.2	35.36	Calibration - multiple
alpha-olefins	Group	132043	23.6	22.24	Calibration - multiple

Table 1: GCxGC report of a PE-rich pyrolysis oil with individual α -olefins as well as a summed total of α -olefins reported.



Conclusion:

The AC custom group type analysis for waste plastic pyrolysis oil of PE and PP is an easy-to-use, preconfigured GCxGC-FID application that provides you with the best and simplest out of the box group-type separation on the market today. Moreover, flow modulation removes the need for costly cryogenic gases and less frequent maintenance.

Whether this GC application is suitable for your waste plastic pyrolysis samples is best to be assessed and discussed on a case-by-case basis. PAC offers the ability to analyze samples in our test lab to verify if this application is suitable for the intended purpose and providing the information needed.

PAC is a leader in standardization and is actively involved in standardizing our concept for analyzing the composition of middle distillates and has published ASTM method for GCxGC-FID, "D8369-22 Standard test Method for Group Types Quantification of Hydrocarbons in Hydrocarbon Liquids with a Boiling point between 36°C and 343°C by flow Modulated GCxGC FID".



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