



APPLICATION HIGHLIGHT:

Waste Plastic Pyrolysis Oil: AC Reformulyzer M4[®] Prefrac Analysis



Introduction:

With the global increase in human population, rapid economic growth, continued urbanization and lifestyle changes, the production and consumption of plastic waste is increasing rapidly. This has a significant impact on human health and causes environmental pollution due to the fact that plastic waste cannot be decomposed by natural organisms and takes hundreds of years to decompose. There is therefore a need and drive for a sustainable transformation of the global economy. The current petrochemical industry, as one of the players in the circular economy, is challenged by the use of waste as a raw feedstock material.

A commonly used technique to process plastic waste is pyrolysis. Pyrolysis converts plastic waste into solid, liquid, or gaseous fuel via the thermal breakdown of long-chain polymers into lighter products in the absence of oxygen. One of the main reaction products is "Waste Plastic Pyrolysis Oil" (WPPO).



The use of WPPO as a raw material in the chemical industry has its challenges and therefore it is necessary to analyze the product for the composition of the chemical group type, in addition to other types of analyzes such as measurements of impurities, boiling point distribution, testing of physical properties, etc..

Analytical Challenges & Method:

WPPO is a liquid product with a wide boiling point range, with a significant amount of lighter components. The final boiling point can vary widely and can exceed 700°C (≈1300°F). With this wide boiling range, it is obviously impossible to analyze the complete chemical composition of the product, due to the enormous numbers of isomers. However, analysis of the light fraction can provide insight into the yield hydrocarbons that can be used as fuel or feedstock for new plastics production.

The AC Reformulyzer M4® is the proven multidimensional GC analyzer for the determination of hydrocarbon group types and oxygenates in gasoline and gasoline feedstock products. It is compliant with ASTM D6839 and ISO 22854 and listed in various global gasoline fuel specifications.

The AC Reformulyzer M4® is also available with the prefractionator option, extending its standard capabilities. The option allows the user to analyze the PIONA composition of the light end (up to C12) in heavier hydrocarbon products, such as WPPO. The heavy fraction itself is not analyzed; it is separated from the lighter fraction of the sample and backflushed to vent.

With this option on the Reformulyzer the user can analyze the WPPO and receive group type information (up to C12) of the product and in addition the light end fraction percentage.

Principal of the AC Reformulyzer M4® Prefrac:

The Reformulyzer M4 Prefrac has a dual inlet system, consisting of a PTV (Temperature Programmable Vaporizer) injector with a pre-column liner inside, coupled to the standard Split/Splitless (S/SL) inlet of the Reformulyzer.

The regular Reformulyzer M4 analysis of samples (including oxygenates) in the Gasoline boiling range (FBP up to 225°C) can be obtained while injecting on the S/SL injector.

Heavy samples, such as the WPPO, are injected on the PTV injector in Prefrac mode only. The sample will first undergo a boiling point pre-separation on the pre-column liner. The light fraction (up to C12) of the sample is directed to the S/SL inlet for separation on the Reformulyzer.

By a timed valve switch, the heavy part of the sample is back flushed from the pre-column to a vent. Preventing the heavy part from entering the Reformulyzer M4 system. This pre-separation technique is an industry proven configuration used in the AC DHA combi analyzer for more than 20 years.

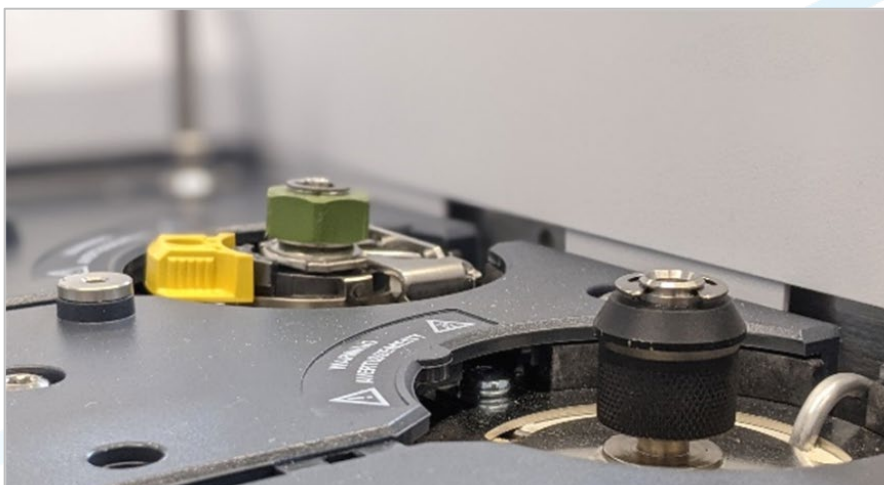


Figure 1: Split & PTV inlet on M4 prefrac.



The main advantage of this new configuration, based on the M4, is the fact that the full standard capabilities of the AC Reformulyzer M4® remain the same. And it can therefore also be used for regular analysis of gasoline and gasoline raw materials.

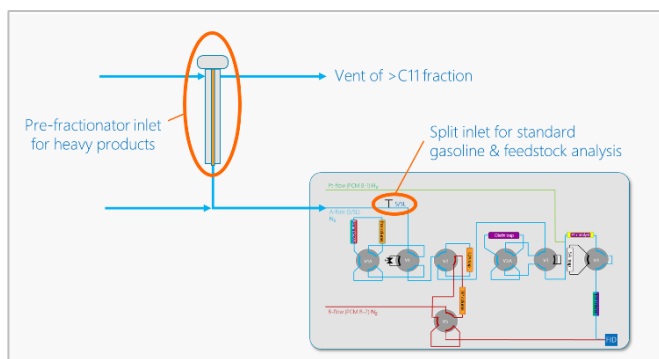


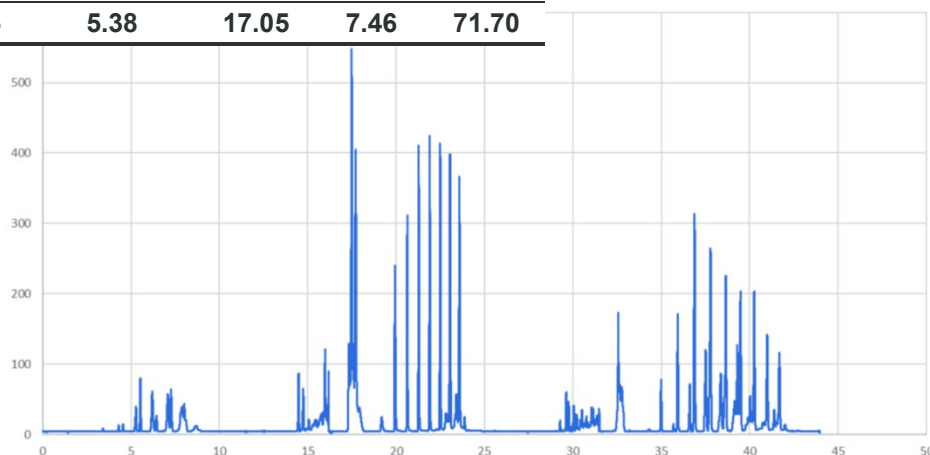
Figure 2: Simplified flow diagram of AC Reformulyzer M4® configuration.

Figure 3: AC Reformulyzer M4® Prefrac.

Example Data:

Below, two examples of different types of WPPO analyzed on the AC Reformulyzer M4® configured with the prefractionation option.

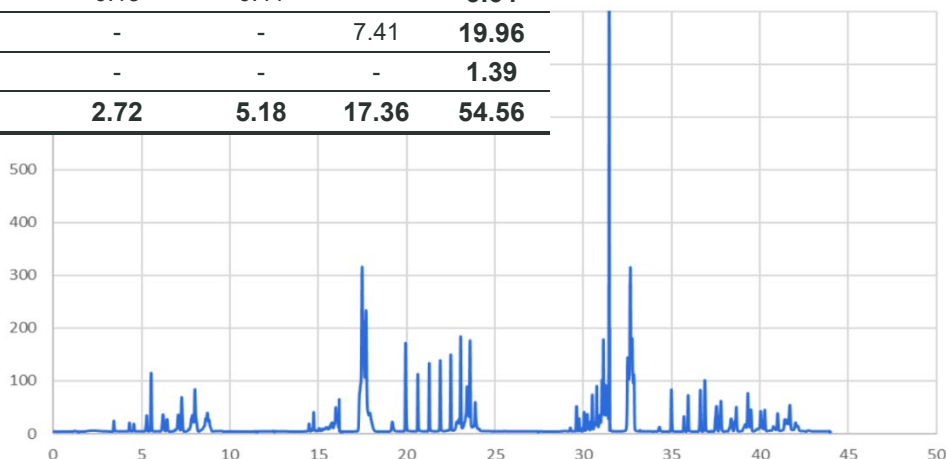
Cnr	Naph.	i-Par.	n-Par.	Cyclo Ol.	Olef.	Arom.	Total
4	-	0.03	0.30	-	0.59	-	0.92
5	0.06	0.07	1.73	0.07	1.23	-	3.16
6	0.33	0.57	1.86	0.57	2.83	0.53	6.68
7	0.75	0.22	2.51	1.39	2.74	0.55	8.16
8	0.78	0.63	2.72	1.30	2.46	0.88	8.78
9	0.87	0.62	2.77	0.83	3.35	0.99	9.43
10	0.60	0.26	2.93	0.93	2.21	1.46	8.39
11	0.24	0.56	2.83	0.27	1.65	-	5.56
12+	-	14.98	-	-	-	3.05	18.03
Poly	2.58	-	-	-	-	-	2.58
Total	6.22	17.95	17.65	5.38	17.05	7.46	71.70





Cnr	Naph.	i-Par.	n-Par.	Cyclo Ol.	Olef.	Arom.	Total
4	-	0.13	0.26	-	0.54	-	0.93
5	0.10	0.09	1.16	0.18	0.48	-	2.02
6	0.25	0.78	0.62	0.56	0.88	0.09	3.18
7	0.39	0.25	0.75	0.65	0.73	0.30	3.07
8	0.48	0.64	0.81	0.41	0.57	0.60	3.52
9	0.68	1.00	0.93	0.26	1.10	1.16	5.13
10	0.78	0.89	1.29	0.50	0.46	7.81	11.73
11	0.43	1.24	1.40	0.15	0.41	-	3.64
12+	-	12.55	-	-	-	7.41	19.96
Poly	1.39	-	-	-	-	-	1.39
Total	4.50	17.58	7.22	2.72	5.18	17.36	54.56

Figure 4: Example data.



General Remarks:

- Results can be reported in weight and volume % (when sample density is known).
- Found results are in line with other type of analysis performed on these samples, like for example:
 - Difference in normal-Paraffin concentration of the sample is shown in Simulated Distillation (SIMDIS) results as well.
 - The found recoveries are in line with the C11 (≈ 200 °C) cut on High Temperature SIMDIS analysis.
 - A lower recovery means that the overall product is considered to be heavier. Which can be an issue in other types of analysis, such as physical distillation.
- Repeatability of a duplicate analysis is proven to be excellent (recovery 71.08 vs. 71.70%).

Conclusion:

The AC Reformulyzer M4® configured with a prefractionator offers the petrochemical industry an excellent tool for analyzing the carbon group types up to C12 (≈ 200 °C) or Waste Plastic Pyrolysis Oils (WPPO). And thereby support the industry in working towards a more circular economy.



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