Reformulyzer M4 with sample pre-fractionation option

- Group type separation beyond scope of ASTM D6839 / ISO 22854
- Analyze products with FBP up to 525 ˚C / 977 ˚F
- Standard Reformulyzer capabilities
- Industry proven configuration

Keywords: Reformulyzer M4, group type analysis, prefractionation, contamination

Introduction

Refinery laboratories can be faced with the question to analyze gasoline or gasoline feedstock products which are contaminated or "out of spec". This can for example be the case when a unit or section of the plant has a malfunction or an upset.

Part of the usual procedures within the mitigation protocols, is for the lab to refrain from using their standard (Group Type) analyzers as they can be contaminated with the heavier material. Contaminating the current pool of group type of analyzers will put at risk the day-to-day analysis of the standard products.

AC Analytical Controls' analytical solution the AC Reformulyzer M4® prefrac (prefractionator), has been recently introduced into the market and it has been engineered to be used as a tool in these circumstances. 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 Reformulyzer is now optionally 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 hydrocarbon products with a maximum Final Boiling Point of 525 ˚C / 977 ˚F. The heavy fraction 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 contaminated or out-of-spec products, without the risk of contaminating the analyzer, and serve the refinery operators by providing group type information (up to C12) of the contaminated product and in addition the light end fraction percentage.

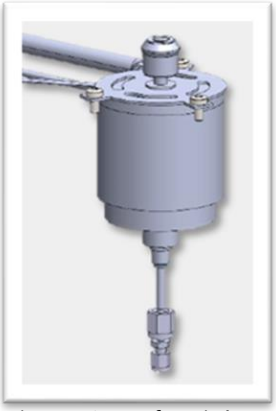

Figure 1: Prefrac inlet

Principle of 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.

Figure 2: Split & PTV inlet on M4 prefrac.

Heavy samples with a FBP up to 525 °C 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.

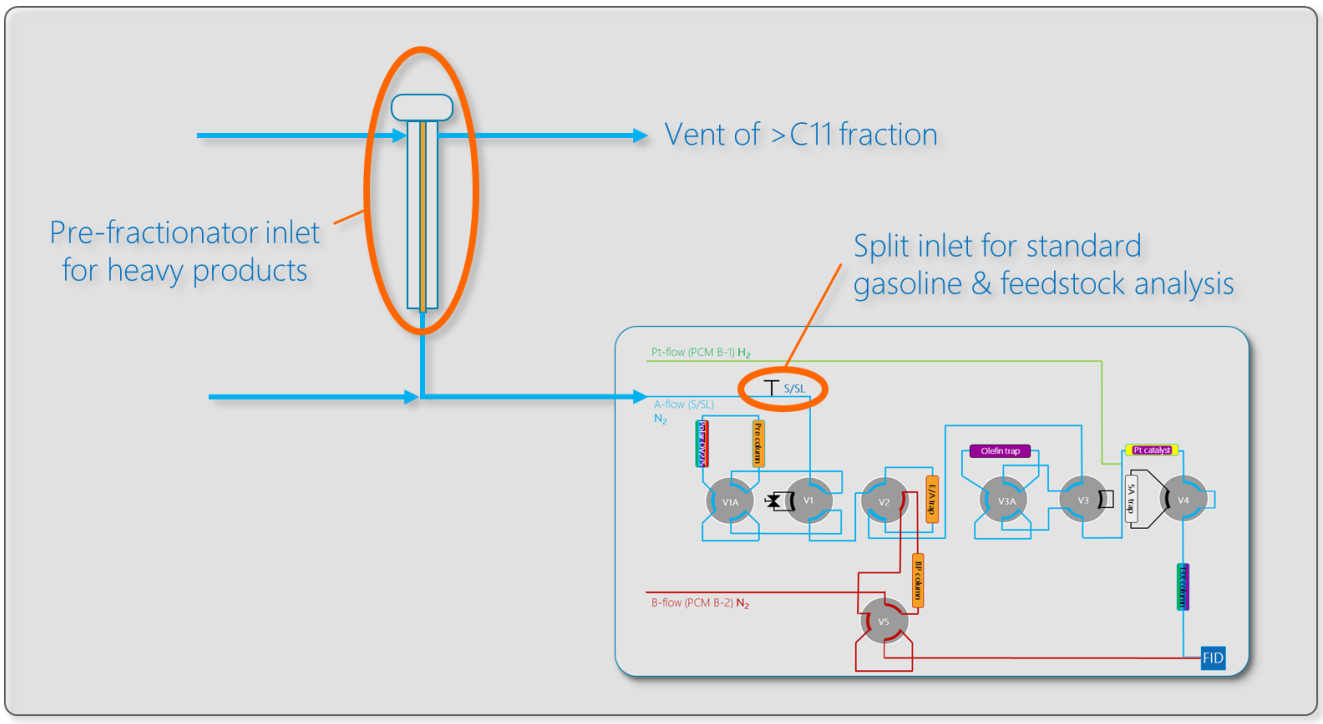

Figure 3: Simplified flow diagram of Reformulyzer M4 configuration

By a timed valve switch, the heavy part of the sample is backflushed 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.

Main advantage of this new configuration based on the M4, is the fact that the full standard capabilities of the AC Reformulyzer M4 remains the same. On earlier generations of the PIONA Prefrac, one could not analyze regular gasolines containing oxygenates. With the new configuration this is no longer an issue.

Quantification

Quantification for the straight PIONA samples injected on the S/SL inlet is done by multiplying the found area for each component or group by its theoretical response factors and the total is normalized to 100% (formulas shown below) as described by ASTM D6839 and ISO 22854.

$$M = \frac{A * F * 100}{\sum A * F} \qquad RRF = \frac{[(C_{aw} * C_n) + (H_{aw} * H_n)] * 0.7487}{(C_{aw} * C_n)}$$

Quantification of samples analyzed with the prefractionation methods is done using a basic external calibration method. To calibrate the system a fully eluting sample is analyzed as an external standard; the corresponding found peak areas equal to 100%.

Prefractionator calibration

Recovery:	87.95
High boiling:	12.05
Response factor:	3.7944149e-005
Calibration date/time:	3/2/2020 10:34:10AM
Sample name:	512 PPIONA Calibration
Calibration sample density:	0.80
Sample density:	0.80

Figure 4: Calibration information

Operator:	Admin	Vial:	101
Acquired On:	3/2/2020 11:40:17AM		
Processed On:	3/2/2020 11:40:17AM		
Sample Info:		LIMSID:	
Sample Type:	QC	Reference Name:	Gravimetric blend
Sample Name:	512 PPIONA	Code:	50.16.512
Test Name:	M4 PPIONA		
Instrument Method:	PPIONA		
Data File Name:	C:\CHEM32\1\DATA\D2003\512 PPIONA.D		

Normalized Weight Percent Results

Cnr	Naph.	I-Par.	n-Par.	Cycl Ol.	I-Olef.	n-Olef.	Arom.	Total
4	-	-	-	-	-	-	-	-
5	1.24	-	1.23	-	-	-	-	2.47
6	2.39	2.38	2.30	-	0.03	1.63	2.44	11.17
7	4.84	-	3.99	-	1.86	-	2.48	13.17
8	5.81	5.95	5.74	-	-	-	9.89	27.38
9	4.76	-	5.13	-	-	-	16.71	26.60
10	-	-	4.81	-	-	-	5.58	10.39
11	-	-	3.87	-	-	-	-	3.87
Poly	4.96	-	-	-	-	-	-	4.96
Total	23.99	8.33	27.06	-	1.89	1.63	37.09	100.00

Recovered Weight Results

Cnr	Naph.	I-Par.	n-Par.	Cycl Ol.	I-Olef.	n-Olef.	Arom.	Total
4	-	-	-	-	-	-	-	-
5	1.09	-	1.08	-	-	-	-	2.17
6	2.10	2.09	2.02	-	0.03	1.44	2.15	9.82
7	4.25	-	3.51	-	1.64	-	2.18	11.58
8	5.11	5.24	5.04	-	-	-	8.70	24.08
9	4.19	-	4.51	-	-	-	14.69	23.39
10	-	-	4.23	-	-	-	4.91	9.14
11	-	-	3.40	-	-	-	-	3.40
Poly	4.36	-	-	-	-	-	-	4.36
Total	21.10	7.33	23.80	-	1.66	1.44	32.62	87.95

Figure 5: Typical "prefrac" report

For heavier samples (analyzed in the prefractionation modes) only areas/components up to C12 are found, thus less than the reference sample. The difference between the found area for the external standard and the prefrac sample analysis is used to calculate the recovery. For example, the found area recovery could be 87.35% (like in the example report left).

All found component /group areas are multiplied by their theoretical response factors and normalized to the calculated recovery, like in this case 87.35%. As additional option, the recovered fraction can also be normalized to 100%.

Conclusion

The AC Reformulyzer M4®, being the proven system for gasoline and gasoline feedstock group type analysis, is now available with the sample prefractionation option. The system can not only analyze the regular gasolines and its feedstocks, but also samples which contain heavier components.

With the additional information the Reformulyzer M4 prefrac option generates, the refinery lab will be in a much better position to assist troubleshooting the refinery units and/or refinery operators needs with the unique issues they may encounter.

Part number: AN-2021-C-004