Why Reformulyzer is the preferred analysis technique for gasoline grouptype analysis?

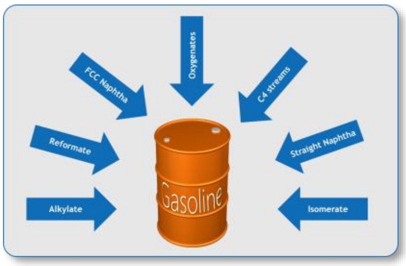
- Direct measurement ensures correct data regardless of sample matrix
- Simple and proven separations
- Use of the industry standard FID: linear & sensitive
- Analysis of gasoline with a variety of ethers & alcohols
- To be used for finished gasoline and blend products
- Referee method in European gasoline specification

Keywords: Reformulyzer, group type, gasoline, direct measurement

Introduction:

Gasoline is a fuel mainly used as an engine fuel for vehicles, and as a retail product it should meet certain specifications based on local or global legislation. The product quality criteria, as listed in the specifications, are for example octane number, RVP, boiling point, and sulfur concentration. These specifications are related to drivability and combustion characteristics as well as environmental parameters.

At the fuel stations gasoline is typically available in different grades, such as regular or premium. The grades indicate the octane rating, which reflects the antiknock properties of the gasoline. In addition, most of the finished gasolines sold today, contain oxygenated components (“oxygenates”) such as ethanol, ETBE or TAME. The oxygenates are added to meet the requirements of renewable fuel standards intended to reduce the greenhouse gas emissions as well as improving the octane rating.



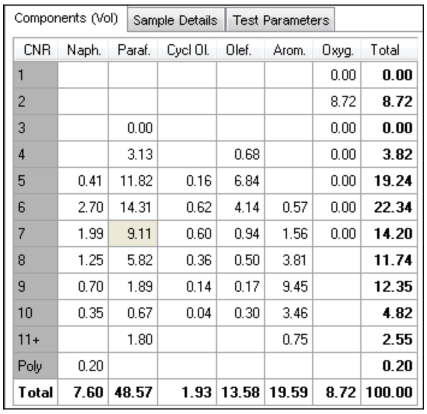
Finished gasoline is a “blend product” consisting of various straight, converted, and other “upgraded” refinery products, such as naphtha, alkylate, isomerate, FCC naphtha, etc. and has a typical carbon number range from C4 to C11. Each hydrocarbon (group) has its own characteristics in terms of octane number, vapor pressure, etc. Gasoline blending is therefore a challenge: the product should meet the specification and for economic reasons at the lowest possible cost.

Based on this carbon number range and the intermediate refinery products used, it is reasonable to conclude that gasoline could consist of more than 1000 components at concentrations varying from trace level up to 10-15% per component. Given the requirements stated in the product specification, as well as the control of all process stages of the refining and blending processes, a reliable and accurate quantitative determination of the various hydrocarbon groups is essential.

This grouptype analysis can be a challenge considering the possible numbers of components and their wide concentration range. The AC Reformulyzer® is the only single analysis method available that separates the full gasoline in the various groups by carbon number. This is the preferred technique compared to single component analysis, where components may not be detected because of their low concentration or are misidentified due to a lack of separation.

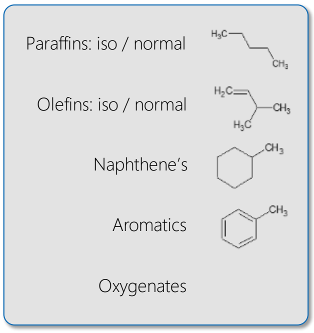
Analysis techniques

Group type analysis for gasoline is to be defined as the quantitative determination of saturates (separated by cyclic & straight/branched), olefins (separated by cyclic & straight/branched), aromatics, and oxygenates all reported either by carbon number or as total. The analysis is not intended to determine individual hydrocarbon components (except benzene, toluene, and oxygenates). See figure 1 as an example.



CNR	Naph.	Paraf.	Cycl Ol.	Olef.	Arom.	Oxyg.	Total
1						0.00	**0.00**
2						8.72	**8.72**
3		0.00				0.00	**0.00**
4		3.13		0.68		0.00	**3.82**
5	0.41	11.82	0.16	6.84		0.00	**19.24**
6	2.70	14.31	0.62	4.14	0.57	0.00	**22.34**
7	1.99	9.11	0.60	0.94	1.56	0.00	**14.20**
8	1.25	5.82	0.36	0.50	3.81		**11.74**
9	0.70	1.89	0.14	0.17	9.45		**12.35**
10	0.35	0.67	0.04	0.30	3.46		**4.82**
11+		1.80			0.75		**2.55**
Poly	0.20						**0.20**
Total	**7.60**	**48.57**	**1.93**	**13.58**	**19.59**	**8.72**	**100.00**

Figure 1: typical gasoline analysis grouptype report



There are multiple chromatography methods to determine the group type composition of the gasoline:

- Single groups/components. These are methods that only analyze a single or specific group of components and not the entire composition. For example, commonly used methods are ASTM D3606, D4815 and D5580. As these method do not report the full sample compositon, multiple analyses are needed to achieve that.
- Methods that (try to) analyze all individual components in a sample, like DHA. Group type concentrations are calculated by summing individual components identified and quantified. Although a high resolution column has a high resolving power and a high peak capacity, an important source of error in this method is coelution of compounds of different classes. It is apparent that there is ample overlap of peaks of different classes, especially if the sample contains relatively high concentrations of olefins.
- Single column analysis using special detection techniques to overcome separation and/or identification issues. These so called hyphenated systems (single column separtion with correlation based detection) may improve identification but typically:
    - have sensitivity and linearity issues. Therefore they are not reliable in quantifying components at low concentrations, or run out of linearity for higher concentrations.
    - only partially resolve co-elutions.
    - have deviating response factors for the various hydrocarbon groups or even individual components which significantly affect quantification in case of mis-identification or unresolved co-elutions.
    - rely on completeness of the database used, thereby potentially missing components (such as certain oxgenates) in the overall quantification.

  These shortcomings will result in an inaccurate overall grouptype analysis.
- "Real" group type analysis by multi-dimensional gas-chromatography, as used in the AC Reformulyzer. The system combines simple and robust separation principals, such as:
    - aromatics - non-aromatic separation using a polar column.
    - carbon number and cyclic/paraffinic separation using a molecular sieve column.
    - aromatics and alcohol separation based on boiling point (using a methyl-silicon column).

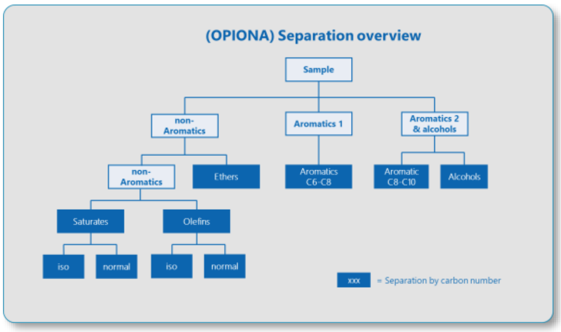


Figure 2: typical gasoline analysis grouptype report

These are straight forward separations with no risk of co-elutions or mis-identification. Figure 2 shows the typical separations taking place in systems.

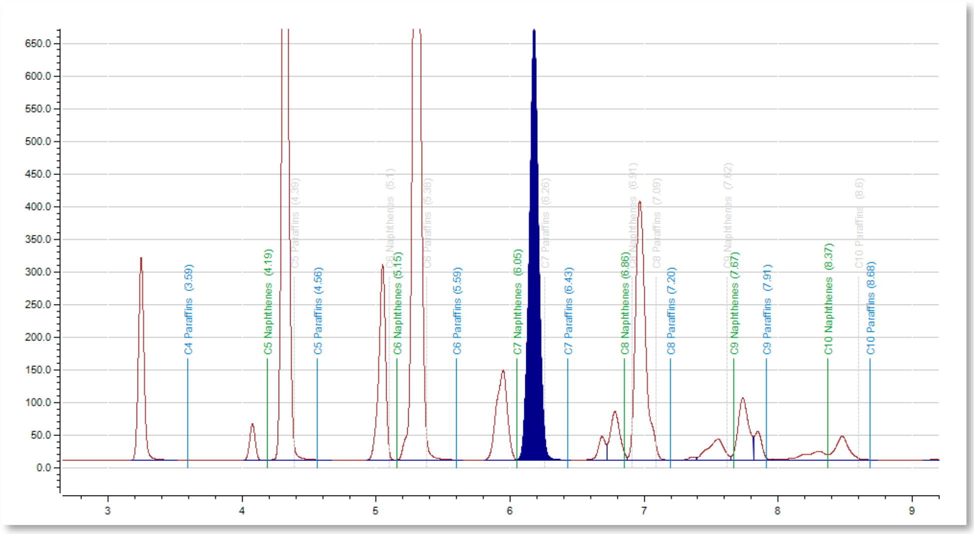


Figure 3: example of separation for the saturated cyclic and paraffinic hydrocarbons by carbon number.

Column temperatures and other setpoint conditions, such as valve timings, are predefined according to the method used and only require evaluation and adjustement due to column aging or in case of specific sample characteristics. Dedicated quantitative & qualitative standards are available to check the system performance.

There are two internationally recognized methods describing this analysis technique: ISO 22854 & ASTM D6839. The ISO 22854 is listed as the referee method for the hydrocarbon type analysis in the European gasoline specification method EN 228.

Group type analysis advantages

Using a true group type analysis, like the Reformulyzer, has several advantages over other techniques:

- One analysis covers the complete grouptype composition. No need for multiple analysis followed by summation of the results. The precision of the results for the full grouptype composition is based on a single analysis, and not the summation of errors of the multiple analysis needed to come to one result.
- As indicated, gasoline can contain a huge number of components in a wide concentration range. Separating the components by group and carbon number has advantages like:
    - components with low concentrations are not missed in the overall results (see figure 4)
    - there is no need to separate and identify all individual components, thus no risk of co-elution and/or related mis-identifcation

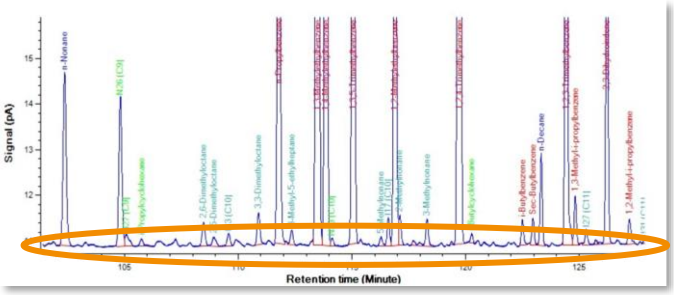


Figure 4: typical ASTM D6730 DHA chromatogram, showing a huge number of components being neglected, and thus missing in the quantification.

- The industry standard FID detection provides robust, sensitive and highly linear detection of all eluted groups. The FID is not concentration sensitive and the detected ions are proportional to the concentration of the organic species. Quantification is based on theoretical response factors. Oxygenate FID factors are determined experimentally.

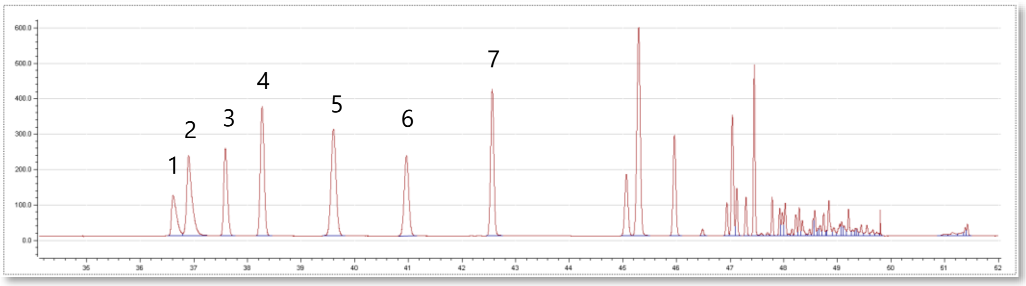
$$\text{RRf} = \frac{[(C_{aw} * C_n) + (H_{aw} * H_n)] * 0.7487}{(C_{aw} * C_n)}$$

Where:

RRf = relative response factor for a hydrocarbon type group of a particular carbon number
C_{aw} = atomic mass of carbon, 12.011
C_n = number of carbon atoms in the hydrocarbon type group, of a particular carbon number
H_{aw} = atomic mass of hydrogen, 1.008
H_n = number of hydrogen atoms in the hydrocarbon type group of a particular carbon number
0.7487 = factor to normalize the result to a methane response of unity

Figure 5: Relative Response Factor calculation based on chemical composition

- The results of PTP programs show an excellent comparison with other direct measurement techniques, which is reflected in the various correlations as stated in the ASTM D6839. The Reformulyzer shows no or only a very small bias with methods such as ASTM D5769, D5580, D3606 & D6550. Correlations are available for those cases where a small bias needs to be corrected.
- The Reformulyzer follows the industry trend and is fully capable of analyzing complex mixtures of oxygenates that may be present in high concentrations in the gasoline today. This includes alcohols (like methanol, ethanol & tert-Butylalcohol) as well as a wide range of ethers (like MTBE, ETBE, TAME and TAEE) at concentrations up to ≈15% per component.



1. Methanol
2. Ethanol
3. MTBE
4. ETBE
5. TAME
6. TAEE
7. Toluene

Figure 6: oxygenates analysis on the Reformulyzer

Conclusion

The AC Reformulyzer M4® has proven itself to be the only true grouptype analyser for full gasoline composition analysis. It uses simple and proven separation principles and a Flame Ionisation Detector, which is a reliable and direct detection technique without sample or component specific bias.

The AC Reformulyzer M4® is used all over the world and is listed as the referee method for hydrocarbon type analysis in the European gasoline specification. Since the introduction of Reformulyer in the mid 1990’s as a succesor of the PIONA, many refineries and independent test laboratories today rely on already the 4th generation of the Reformulyzer for true group analysis of not only finished gasoline but also gasoline feedstocks, and have confidence in reporting correct results using the only true grouptype analyzer available in the market.