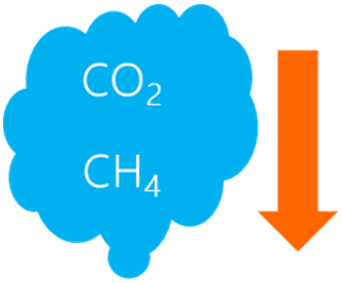
Reformulyzer M4: analysis of gasolines containing various oxygenates

- Full gasoline composition analysis
- Reformulated gasoline meeting latest legislation
- Oxygenates blending to reduce GHG's
- ISO 22854 & ASTM D6839 compliancy

Keywords: Reformulyzer M4, gasoline, oxygenates

Introduction

Gasoline consists of hundreds or more different hydrocarbons, like paraffins, olefins and aromatics, with a boiling range between 30 and 210 °C. Each group has its own characteristics, like aromatics for example have high octane numbers, but, together with olefins, may also increase engine deposits or lead to carcinogenic compound emissions.



Modern gasoline composition and blending is based on various criteria, like vapor pressure and high anti-knock effectiveness, but also low side effects like emission of GHG's (greenhouse gases) and other toxic components. It is therefore that the industry, driven by legislation, is putting effort in reformulating the modern gasolines by blending components that can improve the octane number and at the same time reduce the emission of unwanted components. Adding oxygenated components ("oxygenates") typically result in meeting these requirements. Traditionally oxygenates like ethanol and ETBE are blended, but more and more other oxygenated components are used like alcohols such as methanol and tert-Butanol.

There is a trend in the industry to blend a more diverse mix of oxygenates into the finished gasoline and in higher concentrations than we do today to reduce greenhouse gas emissions.

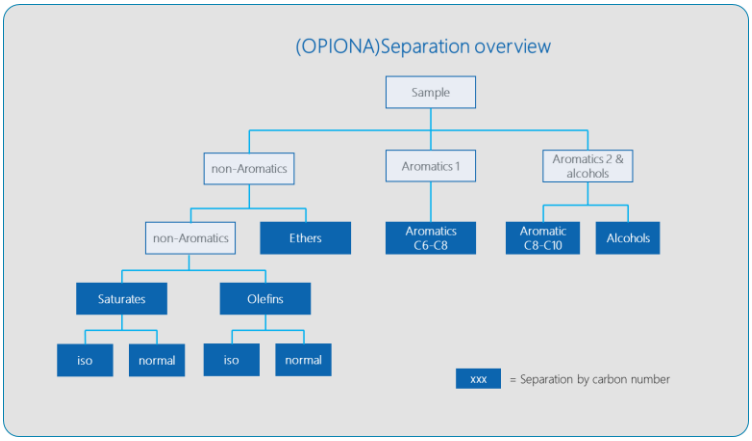
Blending ethers, like MTBE, TAME and TAEE into gasoline has more advantages over ethanol. Using these ethers instead of ethanol result in a more energy-efficient (and thus less CO2 emissions) gasoline. Blending ethanol requires a BOB ("Before Oxygenate Blending" gasoline) with a lower RVP compared to a BOB used to blend ETBE. Producing gasoline with a lower RVP increases energy consumption in a refinery because more processing is required to compensate for the higher RVP of the ethanol.

Legislation defines the requirements for the fuel properties and develops standards for not only these composition criteria, but also how to analyze the fuel. Latest standards of course include the analysis of these oxygenated components.

The AC Reformulyzer ™, in compliance with the latest versions of ISO 22854 and ASTM D6839, is the analyzer to use for analyzing the grouptype composition of the modern gasolines containing one or more oxygenated components.

Principle of Reformulyzer M4

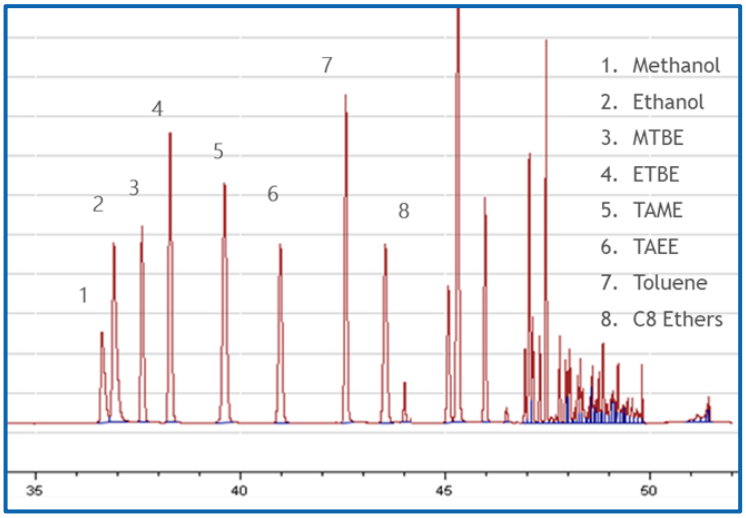
The AC Reformulyzer is based on the proven technology of multi-dimensional gas chromatography. It combines simple and robust separation principles, like separation on polarity for the separation of aromatics from non-aromatics like paraffins & naphthene's or separation on boiling point (chronological by carbon number).



The system uses a Flame Ionization detector, so quantification is based on theoretical relative response factors, and there are no concerns about the linearity (concentration range: 10^7).

Oxygenates analysis

The more complex gasolines containing higher concentrations, and a more diverse mix, of oxygenates, require a different approach in the Reformulyzer M4 to accurately analyze the oxygenates concentrations.



To ensure data integrity and of ease of use, PAC has developed the "Gasoline OXY" mode for the Reformulyzer M4, which has been included with all new systems since 2018. The "Gasoline OXY" mode is an extended version of the standard "Gasoline" mode, optimized to separate the more complex oxygenate mixtures. The mode is optimized to separate all alcohols as well as the heavy ethers (TAME, TAEE, C8 ethers) in one single fraction. This new mode can be implemented to existing Reformulyzer M4 instruments and complies with ISO 22854 and ASTM D6839.

Gasoline OXY vs Gasoline mode

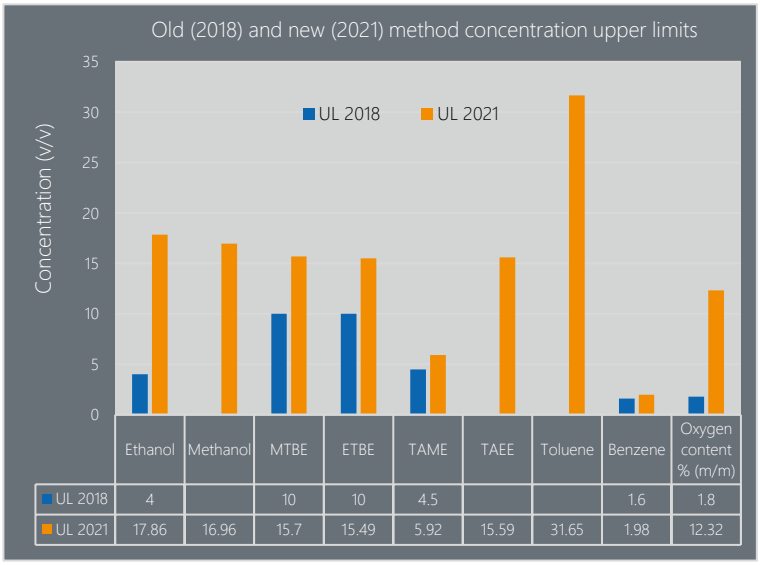
The gasoline OXY mode is intended as a supplemental method next to the regular gasoline mode. The shorter gasoline mode (45 minutes) can be perfectly used for more traditional finished gasolines containing only one or two oxygenates. The gasoline OXY mode (55 minutes) is to be used for all oxygenate blends but is intended to be used if one has the need to analyze a more complex mixtures of oxygenates in a finished gasoline.

Gasoline blends – which mode to use	
Gasoline	**Gasoline OXY**
Single Oxygenate (e.g., ethanol or MTBE only)	Methanol + Ethanol (improved Separation)
Mixture of C4-C6 ethers (e.g., MTBE, ETBE, TAME)	containing TAEE, C8 ethers
MTBE and Ethanol	Ethanol, TAME and or TAEE
ETBE and Ethanol	Mix of multiple alcohols and ethers

ISO 22854 & ASTM D6839 extended measurement ranges

PAC organized an Interlaboratory Study (ILS) in 2020 with the goal to improve and extended the measurement ranges of oxygenates in the ISO 22854 and ASTM D6839. The samples for this ILS were successfully analyzed by 63 participating laboratories from 19 countries using the "Gasoline OXY" mode.

The statistical outcome of the ILS permitted us to update the concentration range for the aromatics, oxygenates and oxygen content for the ASTM D6839 and ISO 22854 method as listed in table 1.



	Ethanol	Methanol	MTBE	ETBE	TAME	TAEE	Toluene	Benzene	Oxygen content % (m/m)
UL 2018	4		10	10	4.5			1.6	1.8
UL 2021	17.86	16.96	15.7	15.49	5.92	15.59	31.65	1.98	12.32

Conclusion

The "Gasoline OXY" mode is proven by the 63 participating laboratories that it is a valuable addition to the available modes for the Reformulyzer M4.

With his new mode the Reformulyzer M4 is capable to analyze more complex mixtures of oxygenates and at higher concentrations which makes the Reformulyzer ready for the future as the increased oxygenate content expected in fuel specifications will fall in the concentration range of the ASTM D6839 and ISO 22854 method.

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