# **APPLICATION NOTE**

ANALYTICAL CONTROLS

## Analysis of E85 Ethanol Fuel Blends using Reformulyzer<sup>®</sup> M4

- Fast Analysis in 39 minutes
- No Sample Dilution

Keywords: *Reformulyzer, Group-Type Analysis, E85 Fuel Blend* 

### INTRODUCTION

With the introduction of the 4<sup>th</sup> generation AC Analytical Controls (AC) Reformulyzer M4, group type analysis of gasolines and its precursors & blend streams has become easier and much faster than before.

The Reformulyzer M4 benefits from the use of capillary/Micropacked columns and traps, resulting in unprecedented speed of analysis, the widest analytical range and excellent precision. It complies with key methods EN ISO 22854 and ASTM D6839 and derived methods.



Depending on the sample stream or product, a range of analytical modes can be used, ensuring shortest possible runtimes, and data as required for that specific product. See Table 1.

This application note describes the quantitative determination of hydrocarbon types and oxygenates in Ethanol Fuel Blends with 85% of Ethanol using the AC Reformulyzer M4.

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Typical Modes used:	PNA	OPNA	PIPNA	PONA	PIONA	PIANO	OPIONA	GASOLINE	FAST GROUP TYPE	E85
Light Straight Run								Ö		
Naphtha	Х		Х			Х				
Heavy Straight Run	.,									
Naphtha	Х		Х			Х				
Depentanized Bottom	Х		Х			Х				
Reformate	Х		Х			Х				
FCC Light/Med/Heavy				Х	Х					
Visbreaker				Х	Х					
Alkylate / Isomerate			Х							
Gasoline Blend							Х	Х	Х	
Gasoline with Oxygenates		Х					Х	Х		
E85, E20										Х
Analysis Time	25	30	30	30	55	40	60	39	15	39
Table 1: Reformulyzer M4 Analysis Modes vs Product Streams					4					

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#### **INSTRUMENTAL**

The determination of different hydrocarbon types and oxygenates is achieved by separation and elution on a series of designed traps and columns. The flow diagram for Reformulyzer M4 is shown below in Figure 1, and the analysis schedule used for this specific method is in Table 2. The Polar Column separates the Paraffins and Naphthenes from the Aromatics while Heavy Aromatics and Alcohols (Ethanol) are retained on the Pre-Column. Ethers pass unretained and are trapped on the Ether/Alcohol-trap to be analyzed on the Boiling Point column. Paraffins and Naphthenes pass the Olefin trap where Olefinic components are trapped. Further separation of Saturates is on the 13X Column resulting in a carbon number distribution.

By using multiple valves and columns the PolyNapthenes and Aromatics, Alcohols are analyzed on a Boiling Point Column in two different Aromatic fractions. Between two aromatic fractions the Olefin trap is desorbed in backflush and Olefins are separated on 13X column. The Micropacked traps and columns are located in the left side and have separate heater elements for individual temperature programming. This allows heating and/or cooling of traps simultaneous, resulting in total analysis runtime of 39 minutes.

From (min)	To (min)	Components	Column route
0	12	C4 to C11 N+P	1 <sup>st</sup> Polar column fraction on 13X Column
12	15	Ethers	Trapped Ethers via E/A-trap to Boiling Point Column
15	16	Saturates > 185°C	Backflush Boiling Point Column
16	26	C4 to C11 CO+O	Backflush desorption of Olefin trap on 13X Column
26	28	C6 to C8 A and pN	2 <sup>nd</sup> Polar Column fraction via E/A-trap to Boiling Point Column
28	39	Saturates > 185°C	Backflush Boiling Point Column of 2 <sup>nd</sup> Polar Column fraction
29	37	Alcohols + C8 to C10 A	3 <sup>rd</sup> Polar Column fraction via E/A-trap to Boiling Point Column
38	39	Aromatics > 185°C	Backflush Boiling Point Column of 3 <sup>rd</sup> Polar Column fraction

Table 2: Reformulyzer M4 Gasoline E85 method

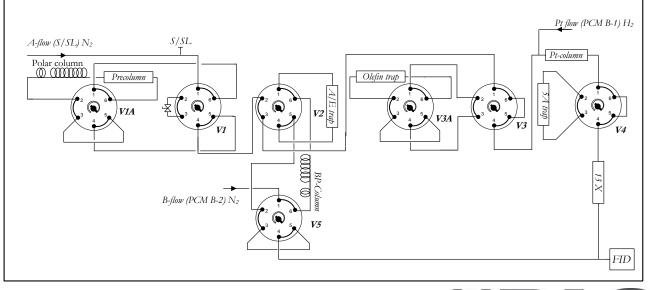


Figure 1: Reformulyzer M4 Flow Diagram

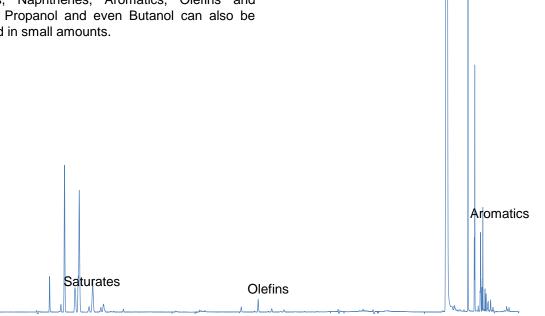




A E85 fuel blend obtained from the field was analyzed undiluted using the Reformulyzer M4 in Gasoline E85 mode.

A Representative chromatogram is shown below and typical report outputs from the analysis for the sample are in Tables 3 and 4.

Chromatogram shows clear group separations for Paraffins, Naphthenes, Aromatics, Olefins and Ethanol. Propanol and even Butanol can also be observed in small amounts.



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0 15 5 10 Figure 3: E85 Fuel Blend in E85 mode

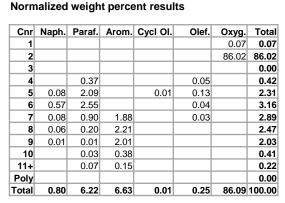


Table 3: Reporting Gasoline E85 Weight%

Normalized volume percent results

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Cnr	Naph.	Paraf.	Arom.	Cycl Ol.	Olef.	Oxyg.	Total
1						0.07	0.07
2						85.45	85.45
3							0.00
4		0.49			0.06		0.55
5	0.09	2.49		0.01	0.16		2.75
6	0.60	3.06			0.04		3.70
7	0.08	1.09	1.62		0.03		2.82
8	0.06	0.24	1.99				2.29
9	0.01	0.01	1.82				1.84
10		0.03	0.34				0.37
11+		0.07	0.09				0.16
Poly							0.00
Total	0.84	7.48	5.86	0.01	0.29	85.52	100.00

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Table 4: Reporting Gasoline E85 Volume%



Reported compositions Weight% are in and Volume%.

EtOH



### CONCLUSION

The Reformulyzer M4 provides reports group type data in full accordance with key methods EN ISO 22854 and ASTM D6839.

Weight% and Volume% profile reports are generated grouping naphthenes, paraffins, olefins, aromatics and oxygenates by carbon number as well as the totals of the different groups and the totals by carbon number. Through the use of Capillary and Micropacked columns and Traps The Reformulyzer M4 takes only 39 minutes to produce reliable results in E85 mode.

#### Specifications

Scope / Finished gasoline Paraffins C4-C11 Separation Range Reformer feed Isoparaffins C4-C11 Reformate Olefins C4-C11 Straight naphtha Naphthenes C5-C11 FCC naphtha/Olefins Aromatics C6-C11 Isomerates Oxygenates C1-C6 (includes Methanol, Alkylate Ethanol, n-Propanol, i-Propanol, t-Butanol, E20+/E85 i-Butanol, 2-Butanol, tert-amvlalcohol, MTBE, ETBE, DIPE, TAME) Method Compliance According Methods ASTM D6839, EN-ISO22854, ASTM D5443, IP566, SH/T 0741, GB/T 28768-2012 Ordering Information CCG3500A Reformulyzer M4 110V CCG3500B Reformulyzer M4 200V CCG3500C Reformulyzer M4 230V

Table 5: Reformulyzer M4 Specifications & Ordering Information

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer ®, SimDis, Hi-Speed RGA and Customized instruments.

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