thermo scientific

APPLICATION NOTE

SOLA iQ Trace Analyzer

Analyzer in reforming and isomerization

Keywords

- Thermo Scientific™ SOLA iQ Trace analyzer
- Isomerization
- Reforming
- Sulfur

Introduction

Isomerization and reforming are important processes that occur during petroleum refining. Each of these processes employ catalysts. The total sulfur content of reforming and isomerization feeds is typically controlled to less than 0.5 ppm to prevent catalyst poisoning. Catalyst poisoning is known to reduce the product yields for reforming and isomerization processes. Online measurement of total sulfur in reforming and isomerization feeds provides the information necessary to prevent catalyst poisoning, thereby, ensuring maximum product yield and optimum product quality. The Thermo Scientific SOLA iQ Trace analyzer provides reliable online total sulfur measurements by pulsed ultraviolet fluorescence (PUVF) with detection limits as low as 25 ppb.

The Thermo Scientific SOLA iQ Trace analyzer with sulfur detection limits as low as 25 parts per billion (ppb)

Isomerization

Isomerization processes rearrange straight chain hydrocarbons to branched isomers. One isomerization process utilizes a n-butane rich feedstock. In this case, the goal is to convert n-butane to isobutane. The iso-butane is then utilized as a feed component to other refining processes, such as alkylation. Light straight run naphtha is a typical feedstock for a common isomerization process. Variations of this isomerization process include benzene hydrogenation capability to meet reformulated gasoline specifications. All isomerization feeds are desulfurized to prevent catalyst poisoning. Isomerization of light straight run naphtha results in a valuable, high octane, low sulfur, gasoline blend component.[1] Figure 1 shows the typical location of a SOLA iQ Trace analyzer in the isomerization process.

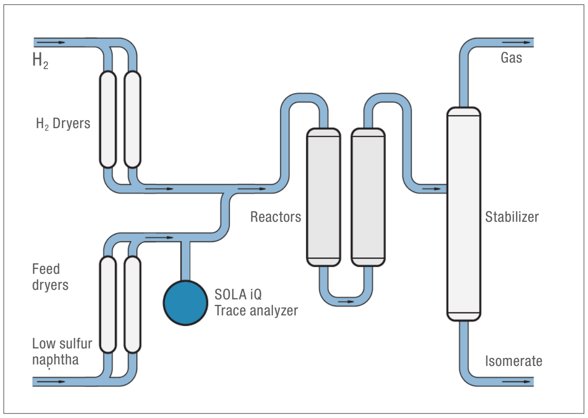

Figure 1. Location of SOLA iQ Trace analyzer in Isomerisation Process

ThermoFisher SCIENTIFIC

Reforming

Catalytic reforming of naphtha boiling range hydrocarbons, typically C5 to C21 paraffins, naphthenes, and aromatics, is used to produce aromatic intermediates for the petrochemical feedstocks and high octane, low sulfur, components for the gasoline pool. Normally rich in paraffins and naphthenes, feedstocks undergo a variety of mainly endothermic conversion processes. These processes include "dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins, isomerization of paraffins and naphthenes, dealkylation of alkylaromatics, hydrocracking of paraffins to light hydrocarbons and formation of coke."[2] Hydrogen produced in the reforming process is increasingly valuable as refiners work to satisfy the increased hydrogen demand of clean fuel production processes. Figure 2 illustrates the typical location of a SOLA iQ Trace analyzer during reforming.

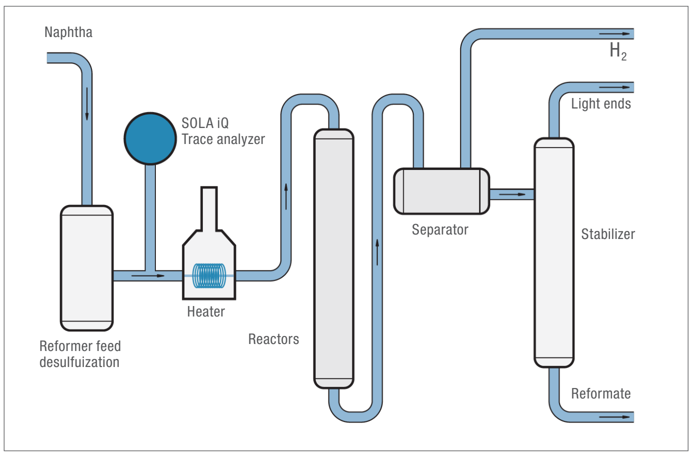

Figure 2. Location of the SOLA iQ Trace analyzer in Reforming Process

The value of online total sulfur measurements

Sulfur in the isomerization feedstock is undesirable because it reduces the activity of the isomerization catalyst by forming metal sulfides.[1] Metal sulfides ultimately reduce the amount of active metal sites needed for the formation of high octane branched chain C5+ isomers.[3] For one isomerization catalyst at 98% C5+ yields, the presence of 133 ppm sulfur reduces the Research Octane Number (RON) to 77 from the RON of 79 observed with no sulfur in the feedstock.[4] Though the formation of metal sulfides is reversible, catalyst regeneration time represents lost production. The sensitivity of reforming catalysts to the adverse effects of sulfur exposure is well known.[5,6,7] Exposure of reforming catalysts to sulfur will generally require higher operating temperatures to maintain the desired product octane number. Sulfur poisoning of reforming catalysts can also reduce C5+ (the valuable gasoline blend component) and H_2 yields.

Exposure of reforming and isomerization catalysts to sulfur results in the reduction of isomerate octane number, higher energy use to maintain reformate octane, the reduction of reforming H_2 yields and reduction of desired product yields. Isomerate, the reformate and alkylate are examples of low sulfur, high octane gasoline blend components used to blend with higher sulfur blend components, such as FCC naphtha. Isomerate, reformate and alkylate are increasingly valuable as refiners struggle to economically comply with low sulfur motor fuel regulations.The economic production of isomerate, reformate and alkylate can directly contribute to the economic production of clean fuels. The SOLA iQ Trace total sulfur analyzer is one tool refiners can use to ensure that isomerization and reforming processes produce maximum product yield and optimum product quality.

SOLA iQ Trace analyzer repeatability and accuracy

The repeatability and linearity of SOLA iQ Trace analyzer total sulfur measurements were verified with a range of synthetic standards of thiophene in iso-octane with Heliox as the carrier gas. Two standards, 0.04 ppm/wt and 2 ppm/wt, were obtained directly from a vendor. Intermediate concentrations were gravimetrically prepared by mass dilution at an independent commercial laboratory. The nominal concentrations for the five standards were 0.04 ppm, 0.5 ppm, 1.0 ppm, 1.5 ppm and 2.0 ppm.

Table 1 shows the nominal and actual concentrations of the five standards.

Table 1. Comparison of nominal and actual sample concentrations

Nominal ppm/wt	Actual ppm/wt
2	2
1.5	1.5559
1	1.0200
0.5	0.5152
0.04	0.04

The system was first calibrated over a 0 -2 ppm/wt range using the 0.04 ppm/wt standard as the Low Calibration Value, and the 2 ppm/wt standard as the High Calibration Value. Sample loop volume for each standard was 1 microliter, injection time was 30 seconds. Each standard was run for 2 hours. In addition, a five hour run was performed on the 0.04 ppm standard, to establish a Lower Detection Limit (LDL) for SOLA iQ.

Table 2. SOLA iQ Trace analytical performance on five synthetic standards

Statistic	Total Sulfur					
	0 ppm	0.04 ppm	0.52 ppm	1.02 ppm	1.56 ppm	2.00 ppm
Average (ppm)	0.0077	0.0362	0.4997	1.0127	1.5559	2.0023
Standard deviation (ppm)	0.0056	0.0054	0.0061	0.0073	0.0128	0.0132
Relative error on 2 ppm value	0.28%	0.27%	0.31%	0.37%	0.64%	0.66%
Number of data points	360	360	360	377	381	360
Data interval (seconds)	20	20	20	20	20	20
Lower detection limit (5 hour data)		17.4 ppb				

Figures 3–5 show the two hour runs for the 0.04 ppm, 1.02 ppm and 2 ppm standards. Based on the five hour run on the 0.04 ppm standard, a Lower Detection Limit of 17.4 ppb was determined.

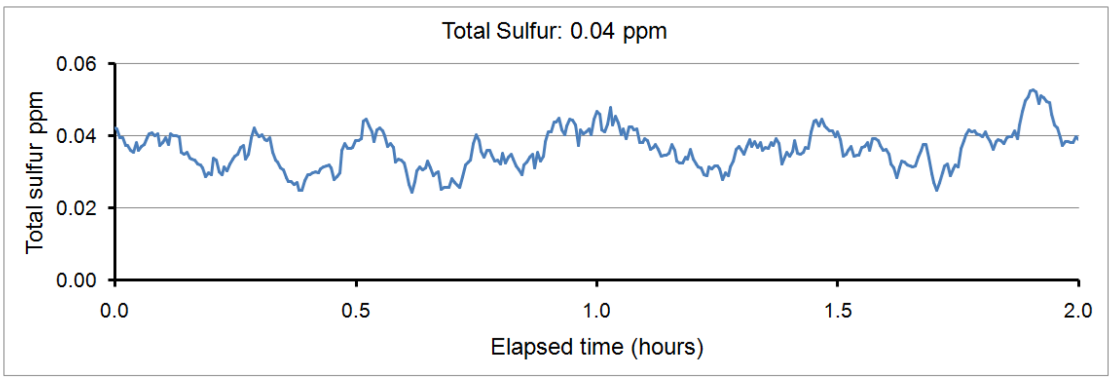

Figure 3. SOLA iQ Trace analytical performance on 0.04 ppm standard over 2 hours

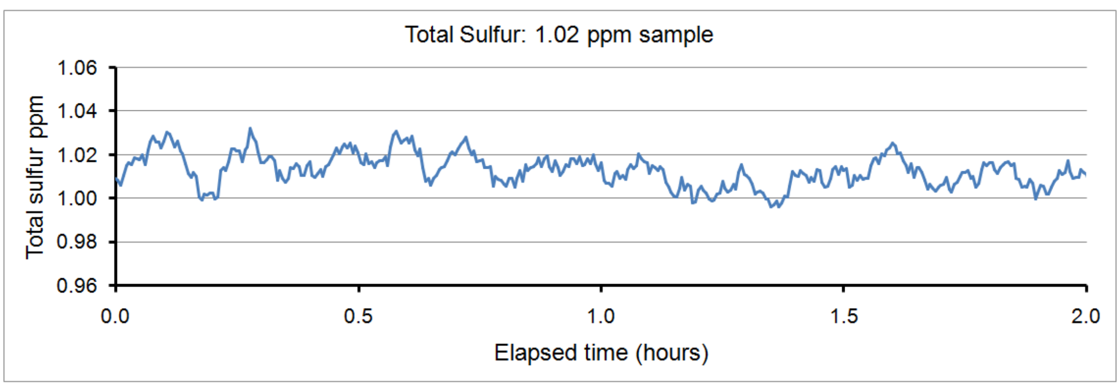

Figure 4. SOLA iQ Trace analytical performance on 1.02 ppm standard over 2 hours

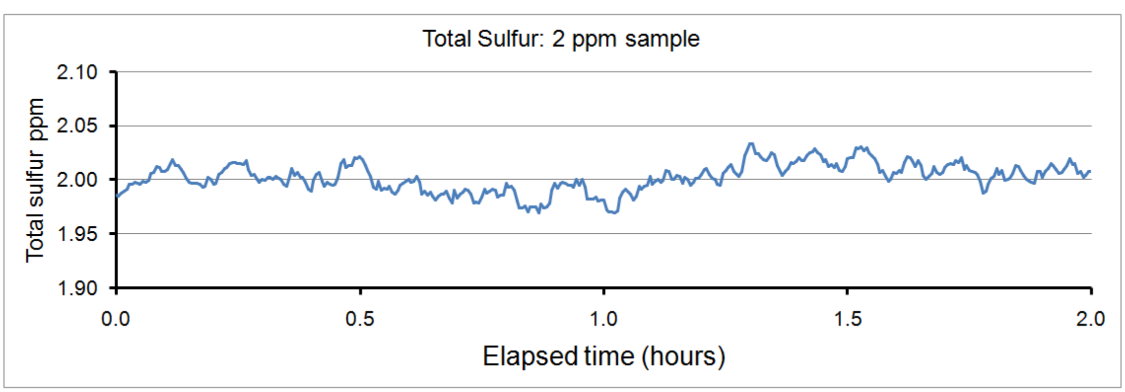

Figure 5. SOLA iQ Trace analytical performance on 2 ppm standard over 2 hours

Figure 6 shows the linearity obtained over the 0–2 ppm range, with a coefficient of determination r2 of 0.999954.

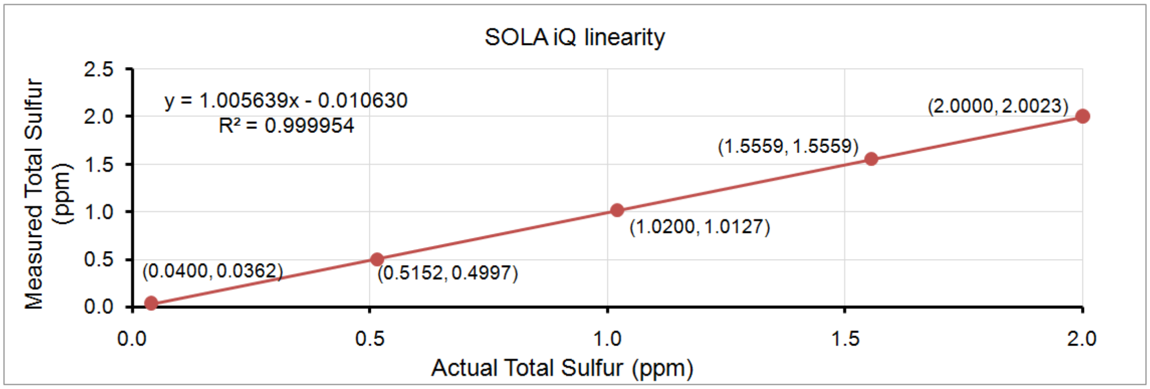

Figure 6. SOLA iQ Trace linearity over 0- 2 ppm range

Conclusions

The SOLA iQ Trace total sulfur analyser has been proven to report very low concentrations of sulfur in a range of liquid and vapor samples, in refinery isomerization and reforming applications it is able to report sulfur with a limit of detection as low as 25 ppb. The continuous, highly stable and linear measurements of the SOLA iQ Trace enable refiners to identify the presence of poisonous sulfur which may lead to degradation of catalyst performance, resulting in lower product yield, quality and plant profitability.

The SOLA iQ Trace uses the same high performance, high reliability Pulsed UV Fluorescence detection system with high temperature sample combustion as other models of SOLA iQ correlating to ASTM D5453, D7551 & D6667, and ISO 20846 and can be applied to a vast range of liquid and vapor samples.

References

1. Meyers, Robert A., Editor-in-Chief, Handbook of Petroleum Refining Processes, Second Ed., The McGraw-Hill Companies, Inc., N.Y., 1997.
2. Russ, Michael R., and Sechrist, Paul A., US Patent 5,614,082.
3. Galperin, Leonid, B., US Patent 5,905,181.
4. Schmidt, R.J., Weiszmann, J.A., and Johnson, J.A., "Catalyst – Key to Low Cost Isomerization", The Oil and Gas Journal, vol. 83, no. 21, pp. 80, 85-88, 1985.
5. Augustine, S.M., Alameddin, G.N., and Sachtler, W.M.H., "The Effect of Re, S, and Cl on the Deactivation of Pt/Y-Al203 Reforming Catalyst", Journal of Catalysis, Vol. 115, pp. 217-232, 1989.
6. Bartholomew, C.H., Agrawal, P.K., and Katzer, J.R., "Sulfur Poisoning of Metals", Advances in Catalysis, Vol. 31, pp. 135-242, 1982.
7. Borgna, A., Garetto, T.F., Monzon, A., and Apestequia, C.R., "Deactivation Model with Residual Activity to Study Thioresistance and Thiotolerance of Naphtha Reforming Catalysts", Journal of Catalysis, Vol. 146, pp. 69-81, 1994

thermo scientific

Specifications for the SOLA iQ Trace analyzer

General specifications	
Detector	Pulsed UV Fluorescence (PUVF) with Pyrolyzer for Total Sulfur Measurement1
Measuring range	SOLA iQ Trace Liquid & Vapor: Full scale ranges from 2ppm to 20ppm—single or dual range analyser, consult factory for alternative ranges
Precision (1x std dev)	SOLA iQ Trace Liquid & Vapor: ≥2ppm ±1% of full scale, two sample injections per minute
Lower limits of detection	SOLA iQ Trace 1.25% of full scale or 25ppb (whichever is greater), defined as 3x standard deviation at low level sample
Linearity	±1% of full scale, two sample injections per minute
Response time	Semi-continuous, outputs updated every 1 second, typically 5-6 minutes to 90% of new value (application dependant)
Number of process streams	Single or multiple (up to 4)—stream selector by others, stream control via SOLA iQ pneumatic outputs
Calibration/validation	Automatic or manual validation, calibration invoked manually or via remote input
Connectivity	
Analog outputs & inputs	4x 4-20mA outputs, 4x inputs (user configurable as 4-20mA or 0-5V)
Serial	4x user configurable RS232 or RS485, TCP/IP Ethernet, MODBUS
Relay & digital outputs	8x relay outputs rated 6A at 240VAC, 8x solid state relay outputs rated at 0.2A at 120VAC/VDC, 12 digital inputs
Pneumatic outputs	For calibration and sample stream selection
Graphical User Interface	Front panel mounted 7” color touchscreen user interface to access analyser functions and diagnostic data including sulfur concentrations, oven and furnace temperatures, PMT and lamp voltages, detector flow rate and more. Connect securely from a remote location on your PC or mobile device to access all front panel display functions.
AutoCONFIG™ software	Security protected access to all analyzer setup and configuration parameters and all process and diagnostic data. Connect via a standard PC across your Local Area Network. Download 30,000 data records (process and analzer functions), typically up to 24 hours of records (user configurable).
Utilities	
Ambient temperature	+12°C to +40°C (+54°F to +104°F)
Analyzer mains power	100 VAC - 240 VAC, 50/60 Hz, 18 amp circuit recommended; 18 amps maximum during warm-up cycle; 7-8 amps once achieving operational temperatures
Cabinet purge air	Minimum 3.8, maximum 6.9 barg , 180-210 L/min (application dependant), Oil Free, -40°C (-40°F) dew point
Carrier and combustion gases	Zero Grade Air maximum 5.5 barg 300 ml/min or Heliox (21% Oxygen) for combustion air—consult factory for application specific advice
Cabinet weights and dimensions	
Zone 1 and Div 1 configurations	Height 1420mm (56"), width 610mm (24"), depth 459mm (18") including top mounted purge control unit—consult factory for mounting details.
Zone 2 and Div 2 configurations	Height 1130mm (45"), width 610mm (24"), depth 459mm (18") purge control unit not fitted—consult factory for mounting details.
Product weight	Approximately 113kg (250lb), typical; with options the estimated weight is 159kg (350lb)
Approvals	
	ATEX Zone 1, Ex db pxb IIC T2/T3 Gb, using X-Purge and Back-up Purge ATEX Zone 2, Ex pzc IIC T2/T3 Gc, using Z-Purge and Backup Purge CSA (W/C & US Mark), Class 1, Div. 1, Group B, C, & D, T2/T3, using X-Purge & Back-up Purge CSA (W/C & US Mark), Class 1, Div. 2, Group B, C, & D, T2/T3, using Z-Purge & Back-up Purge IEC, Zone 1, Ex db pxb IIC T2/T3 Gb, using X-Purge and Back-up Purge IEC, Zone 2, Ex pzc IIC T2/T3 Gc, using Z-Purge and Back-up Purge Japanese Approval for IEC, Zone 1, Ex db pxb IIC T3 Gb, using X-Purge and Back-up Purge (liquid systems only) Japanese Approval for IEC, Zone 2, Ex pzc IIC T3 Gc, using Z-Purge and Back-up Purge (liquid systems only) Japanese Approval for IEC, Zone 1, Ex db pxb IIC T2 Gb, using X-Purge and Back-up Purge (liquid systems only) Japanese Approval for IEC, Zone 2, Ex pzc IIC T2 Gc, using Z-Purge and Back-up Purge (liquid systems only)

USA
27 Forge Parkway
Franklin, MA 02038
Ph: (713) 272-0404
Fax: (713) 272-2273
orders.process.us@thermofisher.com

India
Industrial Unit No.101+130,
Plot No.C-56/1, TTC Industrial
area, MIDC-Turbhe,
New Mumbai 400 703, India
Ph: +91 82 9199 0337
INinfo@thermofisher.com

China
8/F Bldg C of Global Trade Ctr,
No.36, North 3rd Ring Road,
Dong Cheng District
Beijing, China 100013
Ph: +86 10 84193588
info.eid.china@thermofisher.com

Europe
Ion Path, Road Three,
Winsford, Cheshire CW73GA UK
Ph: +44 1606 548700
Fax: +44 1606 548711
sales.epm.uk@thermofisher.com

Learn more at **thermofisher.com/sulfuranalyzers**

ThermoFisher SCIENTIFIC