Application Note: PI.2023.0409

The Thermo Scientific SOLA II Trace in Reforming and Isomerization

Key Words

- SOLA II Trace
- Isomerization
- Reforming
- Sulfur

Introduction

Isomerization and reforming are important examples of processes that manufacture products used in the gasoline pool. 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 II Trace provides reliable online total sulfur measurements by pulsed ultraviolet fluorescence (PUVF) with detection limits as low as 25 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 iso-butane. 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 II Trace in the isomerization process.

Reforming

Catalytic reforming of naphtha boiling range hydrocarbons, typically C_5 to C_{21} 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

The Thermo Scientific SOLA II — with sulfur detection limits as low as 25 parts per billion (ppb)

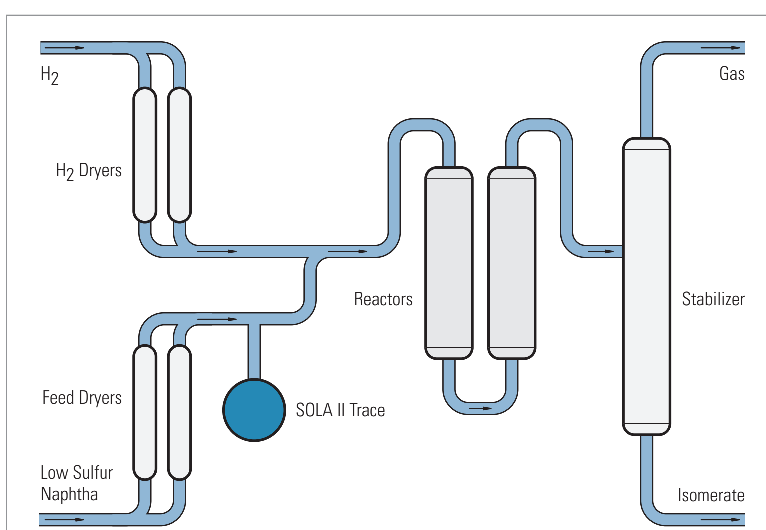

figure 1 – Location of the SOLA II Trace in Isomerization Process

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 II Trace in a reforming process.

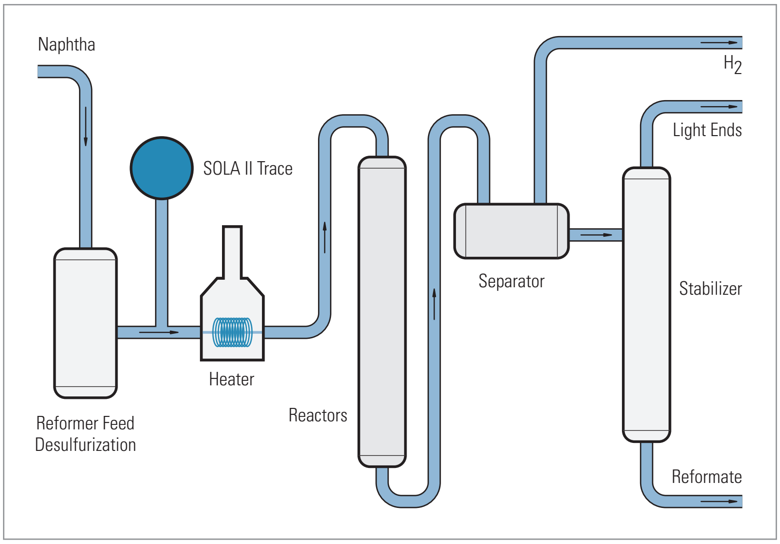

figure 2 – Location of the SOLA II Trace in Reforming Process

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 C_5+ isomers.[3] For one isomerization catalyst at 98% C_5+ 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 C_5+ (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 II 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 II Trace Repeatability and Accuracy

The repeatability and accuracy of SOLA II Trace total sulfur measurements were measured with synthetic samples prepared in high purity, sulfur free p-xylene. Prior to beginning these tests, the SOLA II Trace was calibrated with two known standards containing a non-zero sulfur concentration. The two point calibration is necessary to establish the detector's background reading. For the data presented below, calibration standards containing 137 ppb S (wt/wt) and 1370 ppb S (wt/wt) were used. Each standard was prepared from a thiophene in p-xylene stock solution.

Following calibration, a series of standards were introduced as unknown samples to the online analyzer. The results of these tests are summarized in the tables below.

A sample of 69 ppb S (wt/wt) thiophene in p-xylene was introduced as an unknown sample to the online analyzer. The data collected in *table 1* represents 300 replicates.

A sample of 548 ppb S (wt/wt) thiophene in p-xylene was introduced as an unknown sample to the online analyzer. The data collected in *table 2* represents 120 replicates.

For each of the tests summarized in *tables 1&2*, the Calculated Value represents

Statistic	ppb S (wt/wt)
Average Reported Value	78
Calculated Value	69
Standard Deviation	5

table 1 – Analysis of 69 ppb S (wt/wt) in p-xylene standard

Statistic	ppb S (wt/wt)
Average Reported Value	606
Calculated Value	548
Standard Deviation	11

table 2 – Analysis of 548 ppb S (wt/wt) in p-xylene standard

the gravimetrically determined sulfur concentration. The Average Reported Value represents the average value reported by the online PUVF analyzer. The maximum difference between the average reported value and calculated value, in *tables 1&2*, is 13% for the data presented in *table 1*. For ppb level sulfur determinations, measurement accuracies of less than 15% are generally considered to be excellent results. The standard deviation of each measurement in *tables 1&2* ranges from about 2% - 7% of the calculated value, again excellent results for ppb level sulfur measurements.

SOLA II Trace Repeatability with Low Sulfur Naphtha

A sample of low sulfur naphtha isomerization feed was obtained from a local refinery. The sample was run continuously for a period of 10.5 hours. The results of this study, representing 630 replicates, are presented in *table 3* below. These results suggest that the observed analytical variations are due mainly to random fluctuations.

Statistic	ppb S (wt/wt)
Standard Deviation	4.3
Mean	39.4
Median	39.6
Mode	36.7
Maximum	51.1
Minimum	27.7
Full Scale Value	1540
Repeatability as % FS @ 2 SD	0.6%

table 3 – Analysis of Isomerization Feed Sample #1

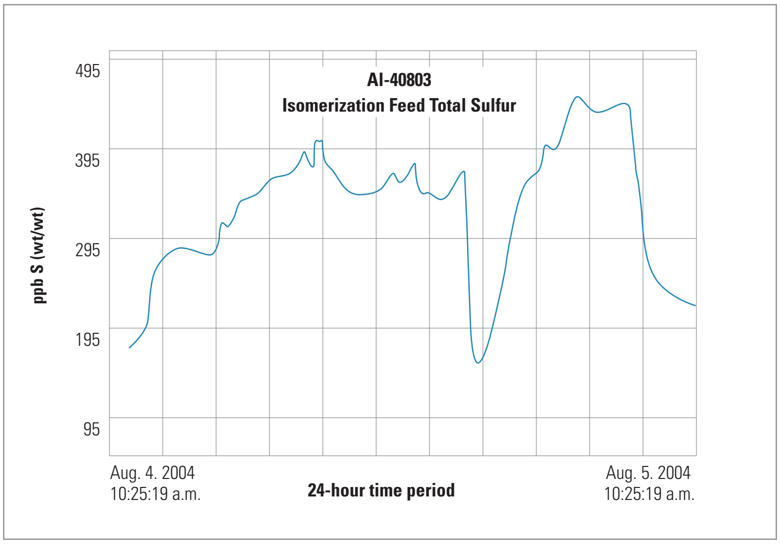

figure 3 – 24-hour Field Run

Field Experience

The SOLA II Trace was proven for trace total sulfur measurements through a six-month field trial on isomerization feed. Data from a continuous 24-hour field run is shown in *figure 3*. The limit for total sulfur in this isomerization feed was 500 ppb S (wt/wt). Examination of *figure 3* shows that the SOLA II rapidly captured some total sulfur excursions near the 500 ppb S (wt/wt) limit. Over a 100 day period, the SOLA II captured two total sulfur excursions of >> 1000 ppb S (wt/wt) and several above 500 ppb S (wt/wt). The process operators quickly reacted to the sulfur excursions, thus, maintaining the desired product yields and quality. The refiner conducting the field trial estimated that the payback on the SOLA II Trace was less than six months, assuming that without it, catalyst poisoning and a reduced octane gasoline pool product could have resulted.

References

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Specifications for the SOLA II Trace (Sulfur Online Analyzer)

General Specifications		
Detector	Pulsed UV Fluorescence (PUVF), with pyrolyzer for Total Sulfur Measurement as SO_2	
Measuring Range	0-2 ppm S (wt/wt)	
Repeatability	Sulfur Concentration:	
	> 500 ppb S	±2.0% RSD at 1 Standard Deviation
	500-400 ppb S	±3.0% RSD at 1 Standard Deviation
	400-200 ppb S	±5.0% RSD at 1 Standard Deviation
	200-100 ppb S	±10.0% RSD at 1 Standard Deviation
	< 100 ppb S	±15.0% RSD at 1 Standard Deviation
Linearity	Equal to or better than repeatability	
Response Time	Semi-continuous, outputs updated every 1 second, 3-5 minutes to 90% of the new value	
Number of Process Streams	Dual streams with auto stream select (optional)	
Calibration	Automatic or manual	
Analog/Discrete Data Communications		
Analog Outputs	4-20 mA DC, one for each stream (dual stream pneumatic outputs optional)	
Alarm Outputs	One global dry contact triggered by one or more of the following: Low sample flow alarm (requires optional sample flow switch in sample system); Low detector flow alarm; Oven/Pyrolyzer temperature fault; Injection valve fault; Purge failure; Calibration fault; Detector temperature fault; Detector lamp voltage fault One out of service dry contact triggered by: Analyzer in calibration; Suspension of analyzer	
Analog Inputs	Optional 4-20 mA DC inputs from density meter for automatic density compensation to achieve measurements in ppm S (wt/wt), (requires existing densitometer or optional densitometer) Optional 4-20 mA DC input from sample flow meter	
Digital Data Communications	Dual channel with the following optional configurations: RS-232 Modbus & RS-485 Modbus; Dual channel RS-485 Modbus; TCP/IP encapsulated Modbus & RS-485 Modbus	
Local MMI	Status of all analyzer parameters (eg. pyrolyzer furnace and analytical oven temperatures, PMT and lamp voltages, detector flow rates, etc.) and analytical results available on the front mounted displays, push button menu access, hazardous area classification remains intact while operating the local display	
SOLA II Modbus Interface	Complete remote control of SOLA II, automatic logging of analysis results and analytical parameters, communication to SOLA II via serial or TCP/IP encapsulated Modbus enables remote diagnostics via modem	
SOLAWeb Remote Interface	Complete remote control of the SOLA II, ability to download 24 hours of analysis results and analyzer parameters, communications to the SOLA II via local area network (TCP/IP) enables remote diagnostics via modem	
System Requirements		
Ambient Temperature	+12°C to +40°C (+60°F to +95°F), +20°C to +30°C to maintain repeatability specifications	
Power	110 VAC, 50/60 Hz at 2000 watts, 20 amps maximum during warm-up cycle 220 VAC, 50/60 Hz at 2000 watts, 17 amps maximum during warm-up cycle	
Certifications	NEC Class 1, Division 2, Group B, C, D NEC Class 1, Division 1 (optional), Group B, C, D CSA/US Class 1, Division 2, Group B, C, D CSA/US Class 1, Division 1 (optional), Group B, C, D ATEX Zone 2, EEx p IIC T2 (T3, T4 optional) ATEX Zone 1 (optional), EEx p IIC T2 (T3, T4 optional) CE Mark	
System Configuration		
Dimensions	1118 mm (44 in) high x 660 mm (25 in) wide x 457 mm (18 in) deep	
Weight	114 kg (250 lb) estimated	

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