

# Process Gas Monitoring in Petroleum Refineries

## Application

Emerson offers several Rosemount Analytical gas analyzer technologies to meet the process control and stream purity monitoring needs of petroleum refineries.

## Background

Gasoline, jet fuel, oils, asphalt and other petrochemicals are all derived from crude oil. Initial distillation separates crude oil into eight component types based on boiling points. These basic components in order of low to high boiling point include:

- Gas - light ends
- Gasoline
- Light and heavy naphtha
- Kerosene
- Light and heavy gas oils
- Lubes
- Asphalt
- Residuals - heavy ends

With gasoline typically being the major processing priority, each component above is subjected to additional value-added processing steps necessary to reach the desired petroleum end-product. The value-added processing may also involve several sequential unit operations.

A summary of these unit operations is summarized below by major crude cuts. See Figure 1.

## Gas – Light Ends

The light end gases are the top cut of crude distillation. Iso and normal butanes ( $C_4H_{10}$ ) and lighter gases such as methane ( $CH_4$ ), ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ) and hydrogen ( $H_2$ ) are then recovered and separated in the refinery gas plant. Typically:

- Hydrogen, methane, and sometimes ethane are diverted to the refinery fuel gas header for use in site heaters and furnaces
- Ethane is used as the chemical feedstock for ethylene upon transfer to a petrochemical complex
- Propane is used for liquefied petroleum gas (LPG) sales or as the chemical feedstock for propylene
- N-butane is used for motor gasoline blending
- Iso-butane is used as feedstock to the alkylation process

Iso-butane is fed with propylene and other cracked gases form heavy gas oil to the alkylation reactor to form gasoline components. The alkylation process occurs with a catalyst of either sulfuric or hydrofluoric acid.

## Light and Heavy Naphtha

After the gasoline distillation cut, the next major crude cut is light and heavy naphtha. The objective of this process step is to increase the octane value of the light naphtha stream. Gasoline components can be converted from light naphtha streams through isomerization units. The isomerization reaction of C4, C5 and C6 fractions occurs over a platinum catalyst.

Aromatics can be retrieved from solvent extraction of the heavy naphtha stream after that cut is first processed in the hydrotreater /reformer units. Heavy naphtha contains undesirable sulfur compounds. In the hydrotreating process, steam and hydrogen are mixed with the heavy naphtha to remove the sulfur. The majority of the sulfur compounds, primarily hydrogen sulfide ( $H_2S$ ), leave with the gas stream. The catalytic reformer process then converts the heavy naphtha to the more desirable paraffins and aromatics.

## Light and Heavy Gas Oil

After the kerosene distillation cut, the light and heavy gas oil cuts are converted to jet or diesel fuel and heating oils. Light gas oil may also contain sulfur. Therefore an additional hydrotreating step is required. The large molecules of the heavy gas oil mix (C8+) are cracked into smaller molecules in the cracking units.

## Lubes, Asphalt and Residuals

The three bottom cuts are the lubes, asphalt and residuals. The lubes are separated first and then directed to the lube plant for final purification and blending. Asphalt and tars are removed at the final major cut point. Column bottoms are collected as residuals and then directed to the coker unit. The majority of the residuals are converted to a coke product.

### Gas Analyzer Applications

In addition to the traditional multi-component process gas analyses typically performed by a process gas chromatograph, there are a number of single component gas measurements found throughout the refinery site. A summary of these applications follow per major unit operation below.

#### Light Naphtha Isomerization Units

A number of gas measurements assists in the process control of isomerization units. Two popular processes are the Penex and TIP (total isomerization process). The objective of these processes is to increase the octane value of the C5/C6 fractions. The reactor effluent passes through a stabilizer unit which separates net gas –hydrogen and light ends. The isomerate or C5/C6 product continues to the gasoline blending areas.

To meet specific environmental gasoline requirements for low benzene levels, the Penex-Plus process was developed to remove benzene from light reformate or naphtha streams by saturating it with hydrogen over a metal catalyst. The Penex-Plus process integrates the benzene saturation step with the isomerization reaction of the Penex process.

Butane (C4) isomerization occurs in a similar process as the C5/C6 isomerization steps. A popular butane isomerization technology process is referred to as the butamer process.

The UOP Company of Des Plaines, IL, is a major licensor of the isomerization and benzene saturation processes.

The reformulated fuel requirements of the Clean Air Act Amendments of 1990 resulted in an increased project activity in the isomerization and benzene saturation areas of the refinery. In California, a number of refineries funded projects of this type commonly referred to as Clean Fuel or Reformulated Gasoline projects.

##### 1) Hydrogen in Make-up Hydrogen Gas to Combined Feed:

Hydrogen is combined with the C5/C6 charge feed to the isomerization reactor. Proper C5/C6: H<sub>2</sub> ratio is controlled by the flow of make-up hydrogen. The content of the make-up hydrogen may vary depending on the operation of various hydrogen recovery units located throughout the refinery.

A typical stream composition may consist of 70 % H<sub>2</sub> with the balance being hydrocarbons. The butamer process has similar process control objectives.

**Solution:** Monitoring the hydrogen concentration of the make-up hydrogen with the Rosemount Analytical X-STREAM flameproof analyzer can assist in controlling the proper feed ratios to the isomerization reactor. A typical operating range is 50 to 100 % H<sub>2</sub> for the penex process and 70 to 100% for the butamer process.

##### 2) Carbon Monoxide and Carbon Dioxide in Make-up

**Hydrogen Gas to Combined Feed:** Hydrogen produced in reforming operations from methane gas contains impurities such as carbon monoxide and carbon dioxide. These impurities can have detrimental effects to many catalyst-based reactions of hydrocarbons such as the type found in the isomerization reactor. Monitoring of CO and CO<sub>2</sub> impurities can help curb these effects.

**Solution:** The Rosemount Analytical X-STREAM flameproof analyzer can meet the needs of this gas monitoring application. A typical operating range is 0 to 100 ppm CO or CO<sub>2</sub>.

##### 3) Hydrogen in Scrubber Off Gas to Refinery Fuel Gas Header:

Monitoring hydrogen in scrubber off gas assists in overall process control of the unit and determines concentration levels for feed to the fuel gas header for use in process heaters and furnaces.

**Solution:** The Rosemount Analytical X-STREAM flameproof analyzer can be used to monitor hydrogen in this application. A typical operating range is 0 to 50 % H<sub>2</sub>. A butamer process net gas scrubber may have an operating range of 20 to 80 % H<sub>2</sub>.

### Catalytic Reforming

The upgrade of heavy naphtha into an aromatics-rich product occurs in the catalytic reforming process. One popular technology is the UOP Company's CCR platforming process. This process has the flexibility to produce either aromatics for downstream petrochemical processes or material for unleaded or reformulated gasoline. In both cases, the process provides a continuous, reliable source of hydrogen.

The reformulated fuel requirements of the Clean Air Act Amendments of 1990 resulted in increased project activity in the catalytic reforming area of the refinery. In California, a number of refineries funded projects of this type commonly referred to as Clean Fuel or Reformulated Gasoline projects.

**4) Hydrogen in Product Separator Recycle Gas:** Hydrogen, in a mixture which is 80 % hydrocarbons, is recycled to the catalytic reformer from a product separator. Monitoring hydrogen in the recycle gas stream assists in overall process control of the unit.

**Solution:** The Rosemount Analytical X-STREAM flameproof analyzer can be used to monitor hydrogen in this application. A typical operating range is 50 to 100% H<sub>2</sub>.

Changing hydrocarbon background composition in this application can result in a change in the total thermal conductivity of the sample without a real change in hydrogen concentration. This effect can result in erroneous hydrogen readings. To improve analyzer accuracy under changing backgrounds, special calibration procedures can be implemented.

For the application above, special zero calibration gas consisting of the following should be utilized:

- 50 % Hydrogen
- 5 % Methane
- 15 % Ethane
- 20 % Propane
- 2.5 % Butanes
- 4 % Pentanes
- 1 % Hexanes

The above component proportions can be varied to match true process conditions.

**5) Hydrogen in Net Gas from Net Gas Knockout Drum:** The net gas knockout drum removes entrained liquids from the reformer gas stream. Monitoring hydrogen in the net gas stream assists in overall process control of the unit and determines concentration levels for feed to the net gas fuel header and the hydrogen-user process units.

**Solution:** The Rosemount Analytical X-STREAM flameproof analyzer can be used to monitor hydrogen in this application. A typical operating range is 10 to 50 % H<sub>2</sub>.

**6) Hydrogen/Hydrocarbons in CCR Nitrogen Header Gas:** Monitoring hydrogen/hydrocarbons in the OCR nitrogen header is important for maintaining nitrogen purity and overall process control. The control and reporting of the make-up and consumption of hydrogen as part of the total plant balance is an important economic consideration in a petroleum refinery.

The monitoring of hydrogen for nitrogen purity in other related applications such as lift gas for fluidized catalytic reactions and surge hopper vents also has similar importance to the refinery.

**Solution:** The Rosemount Analytical X-STREAM flameproof analyzer can be used to monitor hydrogen/hydrocarbons in nitrogen for these applications. The analyzer is calibrated such that 0 % response corresponds to 15 % hydrocarbons in 85 % nitrogen, 50 % response to 100 % nitrogen, and 100 % response to 1 % hydrogen in 99 % nitrogen.

Manual introduction of calibration gases prior to analyzer is provided via toggle operated shut-off valves. Regulating valves maintain calibration gas flow rate. Three calibration gas ports are provided: 1% H<sub>2</sub> in N<sub>2</sub> high span, 100 % N<sub>2</sub> mid-span, and 10.5 % propane, 4.5 % butane, 85 % N<sub>2</sub> zero gas.

## Fluidized Catalytic Cracking

Heavy gas oils and other high boiling materials are selectively converted to higher value products through the fluidized catalytic cracking process. The unit's operation primarily involves reaction with a highly active, two-stage catalyst regeneration in a fluidized bed.

**7) Carbon Monoxide and Oxygen Monitoring of the Fluidized Catalytic Cracking Unit Regenerator Gas:** The waste slipstream of the fluidized catalytic cracking unit regenerator gas is directed to the CO boiler for energy recovery. Monitoring of oxygen and carbon monoxide content aids in proper boiler control and stable operation upon a changing gas stream.

**Solution:** The Rosemount Analytical X-STREAM analyzer meets the CO monitoring needs for this application. A range of 0 to 500 ppm CO is the typical operating range.

The X-STREAM analyzer also meets the O<sub>2</sub> monitoring needs of this application. A range of 0 to 25 % O<sub>2</sub> is the typical operating range.

## Miscellaneous Applications

**8) Oxygen in Hydrocarbon Compressors:** Throughout the refinery, many hydrocarbon streams flow through compressors as feed to the various reactors associated with a specific unit's operation. Air leaks at compressor inlets and diaphragms have the potential to cause an explosive mixture.

**Solution:** Emerson's Rosemount Analytical X-STREAM flameproof analyzer, suited for Class I, Division 1 areas, can monitor the oxygen content of hydrocarbon streams to alert operations of explosive-mixture potential. A typical range for this application is 0 to 25 %.

**9) Total Hydrocarbons in Low Pressure Steam:** Continuous monitoring of total hydrocarbons in low-pressure steam (20 psig) can assist in detecting leaks at counter-current process exchange points such as heat exchangers. Critical leaks resulting from tube failures have detrimental effects on both the process side and steam side systems. Early warning of contamination permits corrective action to prevent costly equipment damage.

**Solution:** Emerson's Rosemount Analytical NGA HFID Heated Hydrocarbon Analyzer, utilizing the flame ionization detection (FID) methodology, is ideally suited for this application. A typical operating range is 0 to 1000 ppm THC calibrated on methane.

**10) Total Hydrocarbon and Oxygen Monitoring of Marine Unloading and Vapor Recovery Operations:** Unloading hydrocarbon product at marine stations along with their associated vapor recovery requires special safety considerations. As vessels are emptied, filled or purged, hydrocarbon vapors have the potential to exceed their explosion limits. On-line gas monitoring enhances safety during these operations.

The monitoring of oxygen content in vapor during marine unloading is required by Coast Guard Regulation 33 CFR 1544.800.

**Solution:** Emerson's Rosemount Analytical X-STREAM flameproof analyzer meets the THC monitoring needs for these applications. A range of 0 to 100 % methane is a typical operating range.

The X-STREAM flameproof analyzer also meets the O<sub>2</sub> monitoring needs of this application. A range of 0 to 25 % O<sub>2</sub> is the typical operating range.

### Continuous Emissions Monitoring Systems (CEMS)

A number of refinery process equipment and stacks are subject to various local and national environmental emissions regulations. Applications typically involve fuel sources such as natural gas, refinery fuel gas, and other process gas streams. Process equipment may involve emissions monitoring of boilers, process heaters, thermal oxidizers, furnaces, selective catalytic reduction units and incinerators.

- 11A. Process Heater/Furnace: Nitrogen Oxides
  - Nitrogen Oxides (NO<sub>x</sub>).....0 to 100 ppm
  - Oxygen (O<sub>2</sub>).....0 to 25 %
  
- 11B. General Boiler/FCC Stack
  - Nitrogen Oxides (NO<sub>x</sub>).....0 to 100 ppm
  - Sulfur Dioxide (SO<sub>2</sub>).....0 to 100 ppm
  - Carbon Monoxide (CO).....0 to 100 ppm
  - Oxygen (O<sub>2</sub>).....0 to 25 %
  
- 11C. SRU (Sulfur Recovery Unit) Incinerator/Tail Gas Stack:
  - Sulfur Dioxide (SO<sub>2</sub>).....0 to 500 ppm
  - Oxygen (O<sub>2</sub>).....0 to 25%
  
- 11D. SCR (Selective Catalytic Reduction) Unit for NO<sub>x</sub> Abatement
  - SCR Inlet: Nitrogen Oxides (NO<sub>x</sub>).....0 to 250 ppm
  - SCR Outlet: Nitrogen Oxides (NO<sub>x</sub>).....0 to 25 ppm
  - Oxygen (O<sub>2</sub>).....0 to 25 %

**Refinery CEMS Applications:** Depending on the site location and applicable environmental CEMS regulations, the following CEMS applications may be found in a typical petroleum refinery:

**Solution:** Emerson can supply either an X-STREAM, MLT Series or NGA CLD analyzer for these applications depending on type of measurements required.

Table 1 - Petroleum Refinery Gas Analyzer Applications

No.	Application	Analyzer Model Selection	Range
<b>Light Naphtha Isomerization Units</b>			
1	H <sub>2</sub> in make-up hydrogen gas to combined feed	X-STREAM	50 to 100 % H <sub>2</sub> (Penex) 70 to 100% H <sub>2</sub> (Butamer)
2	CO and CO <sub>2</sub> in make-up hydrogen gas to combined feed	X-STREAM	0 to 100 ppm CO 0 to 100 ppm CO <sub>2</sub>
3	H <sub>2</sub> in scrubber off gas to refinery fuel gas header	X-STREAM	0 to 50 % H <sub>2</sub> (Penax) 20 to 80 % H <sub>2</sub> (Butamer)
<b>Catalytic Reforming</b>			
4	H <sub>2</sub> in recycle gas from product separator	X-STREAM	50 to 100 % H <sub>2</sub>
5	H <sub>2</sub> in net gas from net gas knock out drum	X-STREAM	10 to 50 % H <sub>2</sub>
6	H <sub>2</sub> /THC in CCR nitrogen header; H <sub>2</sub> in lift gas, H <sub>2</sub> in surge hopper vent	X-STREAM	0 to 1 % H <sub>2</sub> 10 to 50 % H <sub>2</sub>
<b>Fluidized Catalytic Cracking</b>			
7	CO and O <sub>2</sub> monitoring of the fluidized catalytic cracking unit regenerator gas	X-STREAM	0 to 500 ppm CO 0 to 25 % O <sub>2</sub>
<b>Miscellaneous</b>			
8	O <sub>2</sub> in hydrocarbon compressors	X-STREAM	0 to 25 % O <sub>2</sub>
9	THC in Low-Pressure Steam	NGA FID	0 to 1000 ppm THC
10	THC and O <sub>2</sub> monitoring of marine unloading and vapor recovery operations	X-STREAM	0 to 100 % CH <sub>4</sub> 0 to 25 % O <sub>2</sub>
<b>Continuous Emission Monitoring Systems (CEMS)</b>		X-STREAM MLT Series NGA CLD	
11A	Process heater/furnace		0 to 100 ppm NO <sub>x</sub> 0 to 25 % O <sub>2</sub>
11B	General boiler/FCC unit stack		0 to 100 ppm NO <sub>x</sub> 0 to 100 ppm SO <sub>2</sub> 0 to 100 ppm CO 0 to 25 % O <sub>2</sub>
11C	SRU incinerator/tail gas stack		0 to 500 ppm SO <sub>2</sub> 0 to 25 % O <sub>2</sub>
11D	SCR NO <sub>x</sub> abatement unit SCR inlet SCR outlet		0 to 500 ppm NO <sub>x</sub> 0 to 25 ppm NO <sub>x</sub> 0 to 25 % O <sub>2</sub>

## Process Data Information

To ensure qualification of the correct methodology in specifying process gas analyzers in a refinery, it is important to know specific application data information. Process pressures, temperatures, particulate loading and background stream composition are all necessary for the design of a reliable analyzer and associated sample conditioning system.

Changing background gases can interfere with the measurement of the desired gas. For example, the total thermal conductivity of a gas stream may change while the concentration of hydrogen remains the same. Special calibration considerations may be required to compensate for measurements in a changing background stream.

## Sample Handling Requirements

As with any process analyzer application, a proper sample conditioning system is required to obtain an accurate and reliable analysis.

Usually, a gaseous phase sample is conditioned in approximately the following sequence before analysis:

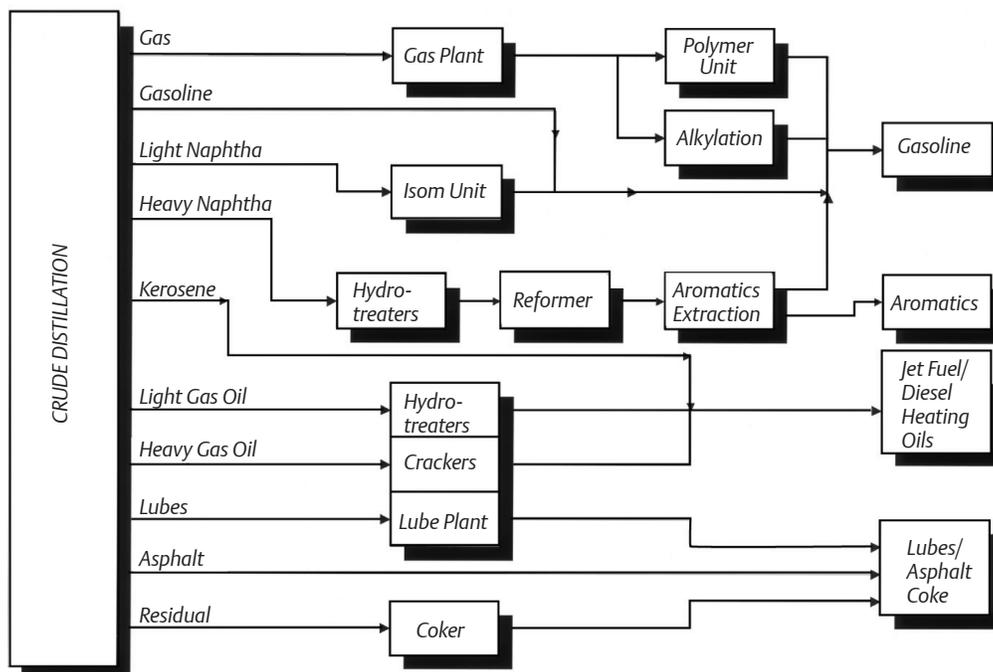
- Initial filtration
- Pressure reduction and control
- Transport to analyzer location
- Multiple stream switching (if required)
- Sample and bypass flow control
- Calibration gas switching (if needed)
- Final guard filtration (if needed)

Maintaining high bypass flow rates relative to the tubing size is an effective means to assure fast equilibration of system and sample. Sample return connections should also be considered. As with any well-designed system, dead-end volume should be kept at a minimum to reduce sample transport lag.

### Sources:

“Refining Handbook,” Hydrocarbon Processing, November 1992  
 Lefler, William L., Petroleum Refining, Penn Well Publishing Company, 1979  
 HPI Market Data, Hydrocarbon Processing, Gulf Publishing Company, 1993.

Figure 1 - Process Gas Analysis in a Petroleum Refinery



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