Process Raman Gas Analysis in Ammonia Production and Refining

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Abstract

On-line process measurement of the composition of gas streams in refining, fertilizer, and other manufacturing industries is essential for the optimal operation of different process units within these facilities. Process analyzers based on gas chromatography, mass spectrometry, and electrochemical technologies are commonly used in these facilities. However, process conditions for certain streams present major challenges for these traditional technologies. Techniques based on optical spectroscopy, including near-infrared (NIR), infrared (dispersive and Fourier transform), and Raman spectroscopy, can provide analysis solutions for these challenging stream conditions. Raman spectroscopy is particularly useful for streams containing homonuclear diatomic gases, such as H_2 and N_2. These gases are key components in many chemical processes involving the creation and use of syngas (H_2, CO, and CO_2), such as the manufacturing of ammonia and methanol. Hydrogen is also an essential feedstock for the hydrotreating, hydrocracking, and catalytic reforming of various hydrocarbon fractions in refineries. A case study will be presented for the application of Raman spectroscopy to analyze syngas from the gasification of petcoke in a fertilizer plant. A second case study will be presented for the analysis of hydrogen, hydrogen sulfide and other compounds in the hydrogen recycle in a refinery hydrotreater/hydrocracker and for hydrogen purity measurements in a hydrogen plant. The discussion will include the overall importance of the measurements to plant operation, and potential cost savings for the Raman measurement technology over other, more traditional technologies. Competitive technologies will be discussed, along with lessons learned concerning the specifics of the Raman analyzer installations, and the unique safety features enabled in implementing this optical technology.

Case 1: Syngas analysis in a fertilizer plant

Coffeyville Resources Nitrogen Fertilizers, LLC, owns and operates a nitrogen fertilizer facility in Coffeyville, Kansas. The plant began operation in 2000 and is the only fertilizer manufacturing facility in North America using a petroleum coke (petcoke) gasification process to produce the hydrogen used in the production of nitrogenous fertilizer. The petcoke is generated at an oil refinery adjacent to the plant, which is also owned and operated by a subsidiary of CVR Energy. The petcoke is gasified to produce hydrogen-rich synthesis gas, which is converted to anhydrous ammonia (NH_3), with over 96% being ultimately converted to the fertilizer, urea ammonium nitrate (UAN) and diesel exhaust fluid (DEF). In 2015, the Coffeyville facility produced 385,400 tons of ammonia and 928,600 tons of UAN solution. Recently, the facility decided to install a new process analyzer using laser-based Raman spectroscopy for the measurement of syngas, due to challenges they had with more conventional process analyzer technologies.

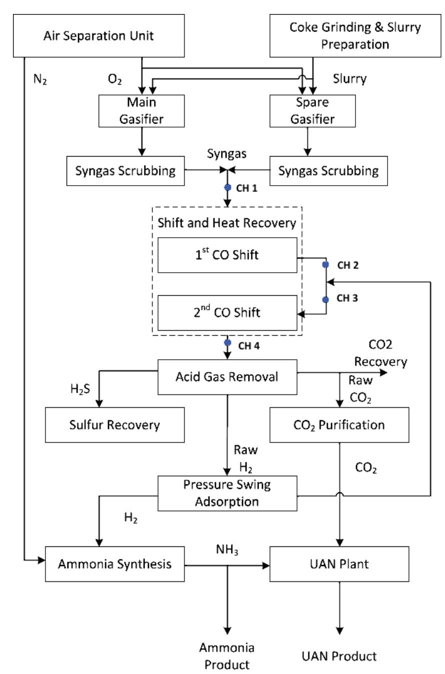

Figure 1. Coffeyville resources process diagram (courtesy of the coffeyville facility)

The Optograf™ analyzer is a process spectrometer that is based on Raman spectroscopy. At this installation, it is installed within the CO sour shift reactor and heat recovery section of the plant. The most important and challenging stream that the analyzer is measuring is the inlet to the first CO sour shift reactor, which essentially represents the composition outlet of the entrained flow slagging gasifier quench section after the scrubbers. This stream presents challenges for analysis as it contains the highest quantity of particulates and water vapor content (as high as 60%). Currently, the composition measurement of this stream is used for monitoring, but not control, of the operation of the gasifier. Two other sample points have been installed and are operational. These are located on the outlet of the first shift reactor and the inlet to the second shift reactor, after the point where a recycle gas stream ties in to the main syngas piping. The fourth sample point will measure syngas from the outlet of the second shift. This measurement will provide the inlet composition of syngas to the acid gas removal section of the facility and is not yet on line as of January 2017. Once the fourth sample point is operational, these four measurements will provide full shift gas analysis.

Table 1. Stream Compositions for the four sample points at the Coffeyville ammonia plant

	Syngas after scrubber	1st Shift Converter Outlet	2nd Shift Converter Inlet	2nd Shift Converter Outlet
Temperature (˚F)	430	825	495	550
Pressure (psig)	600	590	585	580
Cycle Time (min)	4	4	4	4
Hydrogen (%)	33.27	54.62	50.38	55.30
Carbon monoxide (%)	53.85	3.75	13.25	1.10
Carbon dioxide (%)	12.30	40.51	33.87	40.88
Nitrogen (%)	0.53	0.37	1.59	1.74
Hydrogen sulfide (%)	0.77	0.65	0.62	0.66
Methane (%)	0.00	0.04	0.18	0.21
Oxygen/Argon (%)	0.00	0.06	0.11	0.11
Water	Saturated			

All composition values are in mol percent.

The strategy for optimization is centered on a fast compositional analysis. Based on the facility's front end gasifier pressure, relatively fast flow rates occur throughout the shift reactors in the system, so compositional changes can occur quickly, so it is essential that analysis update times are fast. The Raman analyzer can measure all four sample points simultaneously, providing a complete compositional update in four minutes. The monitoring of syngas composition on the outlet of the gasifier allows for potential underlying control opportunities for the gasification process and identifying changes in feedstock composition. While the Raman analyzer installation is still relatively new in the plant and much of the data collected to date has been to establish operational baselines, the fast update time of the analyzer was instrumental in helping the plant identify that rapid changes in the syngas composition after the scrubbers was due to problems in the gasifier quench chamber (reference Figures 1-3 and Table I for the petcoke gasifier process, stream compositions for all four measuring points, and the first sample point composition trend and spectrum).

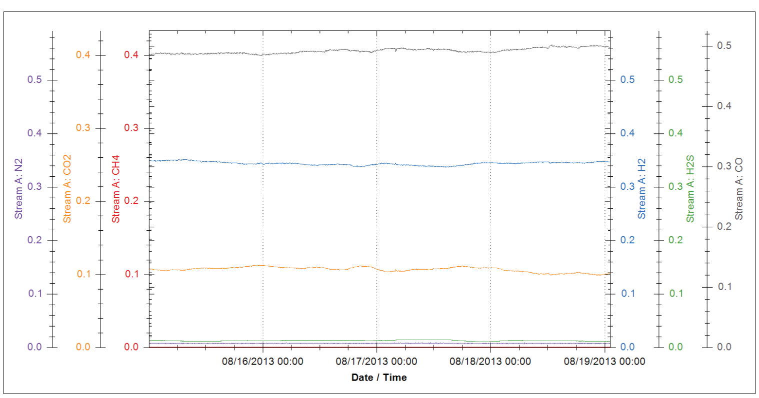

Figure 2. Coffeyville resources stream trend data-syngas after scrubber

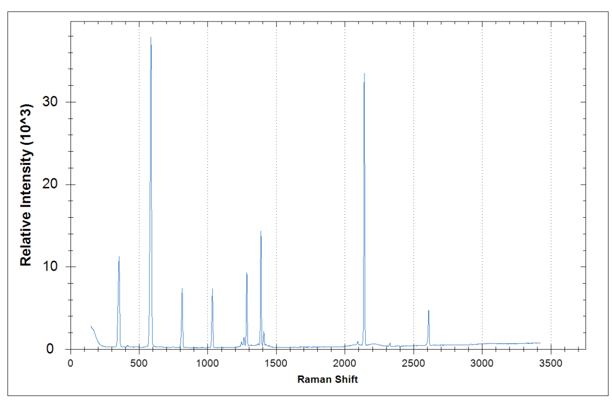

Figure 3. Coffeyville resources spectrum of syngas after scrubber

Case 2: Hydrogen analysis in a refinery

The objective of the refining process is to convert crude oil to gasoline, jet fuel, diesel oil, liquefied petroleum gas and fuel oils. There are many processes within the refinery which utilize hydrogen, including hydrotreating, hydrocracking, catalytic reforming, fluid catalytic cracking (FCC), isomerization, and alkylation. These processes vary depending on the input feed stock and the desired modification to that feedstock, such as sulfur removal, or need to produce specific end products, such as diesel oil. Hydrogen consumption by oil refineries is growing due an increase in global oil consumption, the increasing use of low quality heavy crude oil feedstocks, which requires more hydrogen to refine and due to low sulfur requirements in diesel fuels.

There are several different process units in an oil refinery that are necessary to upgrade or further refine, the primary distillate fractions derived from the Atmospheric Distillation Unit and the Vacuum Distillation Unit. In addition to crude oil and distillate fractions, the use of H_2 is an important consumable used to upgrade some of the distillate fractions, primarily via hydrotreaters (removal of sulfur components) and hydrocrackers (cracking of high molecular weight fractions into smaller molecules). The H_2 is either produced on site (via a hydrogen plant and catalytic reformers) or can be supplied by a 3rd party from a commercial hydrogen/carbon monoxide (HYCO) plant. In most cases, the unused H_2 and other light gases formed in these units are recycled; the recovery of the H_2 is essential for efficient operation of the refinery.

2.1 Recycled hydrogen applications

One west coast refinery is using Raman analysis in the hydrogen recycle processes in their hydrocracking and hydrotreating process units. The typical measurements used to monitor and enhance the operation of the hydrotreater and hydrocracker with the Raman analyzer are recycle hydrogen and hydrogen sulfide content measured before the Acid Gas Removal (AGR) process unit. Key measurement parameters used for the operation of these processes include composition and specific gravity. This measurement is performed to control the hydrocarbon to hydrogen ratio in the reactor which promotes optimal chemistry and prevents coke formation.

Table 2. Stream Compositions for the four sample points at the Coffeyville ammonia plant

	Compressor 1	Compressor 2	Start-up Compressor
Temperature (°F)	120	120	120
Pressure (psig)	1800	2800	280
Cycle Time (min)	2-4	2-4	2-4
Hydrogen (%)	93.0	85.78	93.0
Methane (%)	3.69	5.71	3.69
Ethane (%)	1.10	1.34	1.10
Propane (%)	0.31	1.47	0.31
Iso-Butane (%)	0.07	1.85	0.07
N-Butane (%)	0.07	.85	0.07
Hydrogen sulfide (%)	1.6	0	1.6
Ammonia (%)	0.01	0	0.01
Ethylene (%)	0	0	0
Nitrogen (%)	7.0	1.5	7.0
Iso-Pentane (%)	0.1	0.5	0.1
N-Pentane (%)	0	0.1	0
Hexane+ (%)	0.3	0.5	0.3

All composition values are in mol percent.

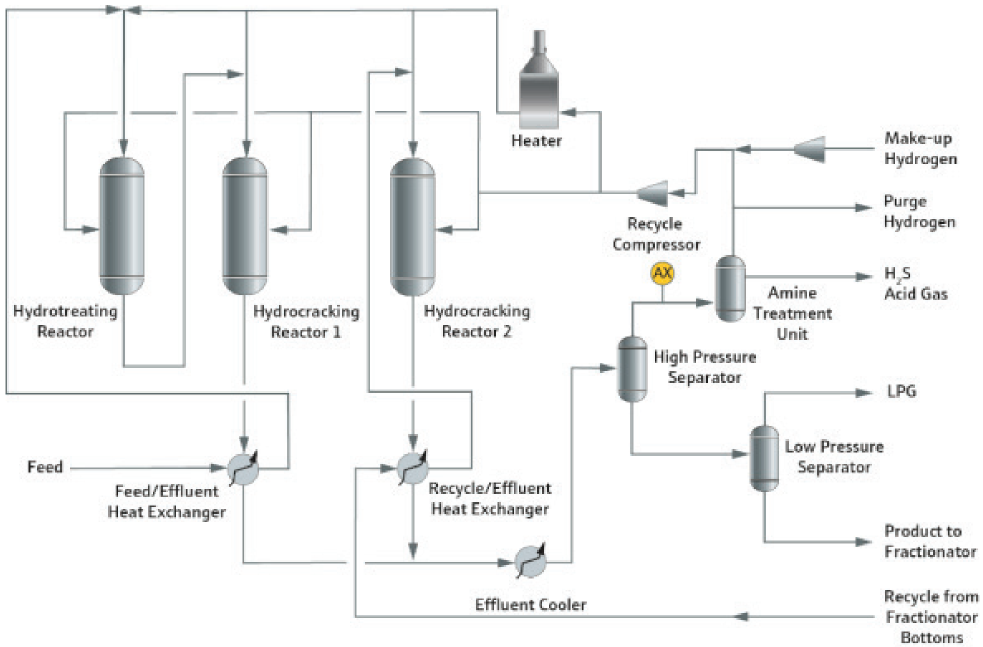

Figure 4. Hydrogen recycle process in hydrocracker showing a typical measurement point

This facility is currently analyzing stream composition in three locations. The first measurement point is at the start-up compressor, which is used only after a catalyst change out in a turnaround period. The goal of this measurement is to help improve process visibility at start-up. This compressor is also used for low pressure cool down. The other two measurement points are upstream of recycle compressors. A typical location for the measurement point is illustrated in Figure 4. Figure 5 shows the changing stream composition over 12 hours in a hydrogen recycle process with output from the Raman analyzer.

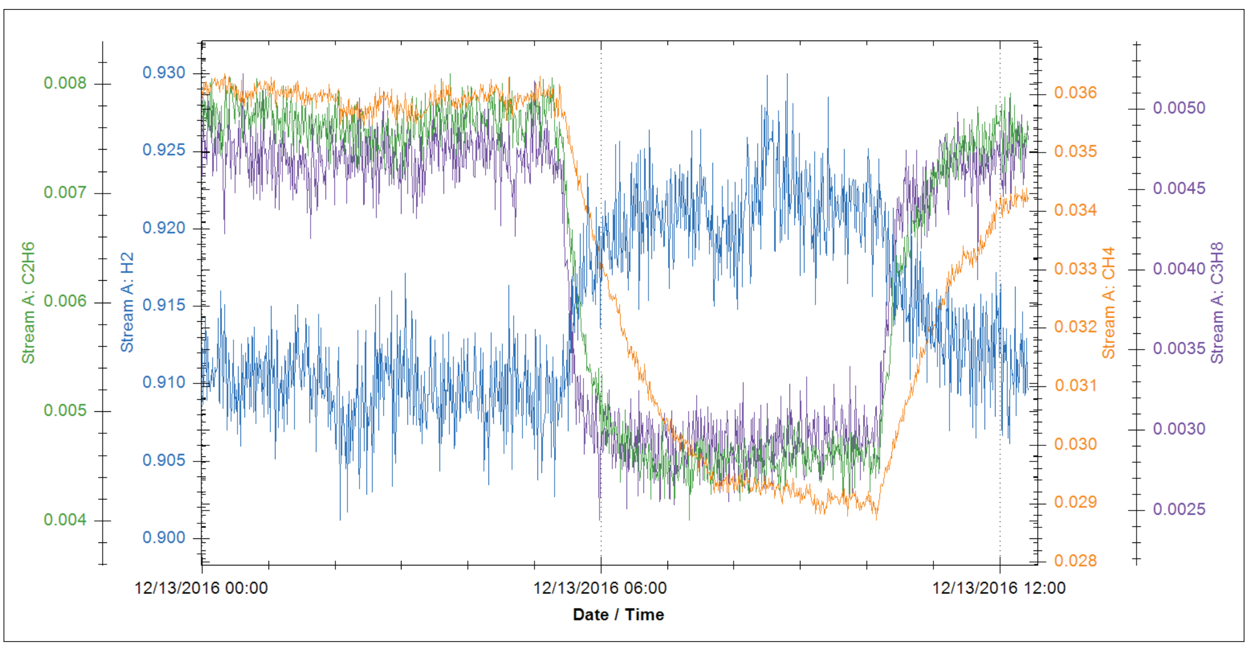

Figure 5. Snapshot of the hydrogen recycle process in a hydrocracker

Prior to installation of the Raman analyzer, this refinery monitored the hydrogen recycle compressors based on the amperage usage of the compressors and specific gravity measurements downstream of the compressors. Now they have process visibility of the composition for the output of the catalyst beds and can more efficiently optimize the process. Process Raman technology is able to report compositional and specific gravity information with as little as two minutes cycle time.

2.2 Captive hydrogen production applications

There are many refineries that produce 'captive' hydrogen for use in numerous hydrotreating and hydrocracking processes that are essential for refinery operation. The majority of this hydrogen is produced via SMR of natural gas inside the refinery battery limits (ISBL). The output of the SMR is syngas, which is a mixture primarily of H_2 and carbon monoxide (CO). The CO in the syngas is combined with water and converted into carbon dioxide (CO_2) and additional H_2 using Water-Shift reactors. When recovery and sequestration of CO_2 are required, further processing purifies the syngas by removing CO_2 via a CO_2 absorber. In many refineries, Pressure Swing Adsorption (PSA) units play a major role in the final H_2 purification process. Figure 6 and Table III illustrate key measurement points in a hydrogen production plant.

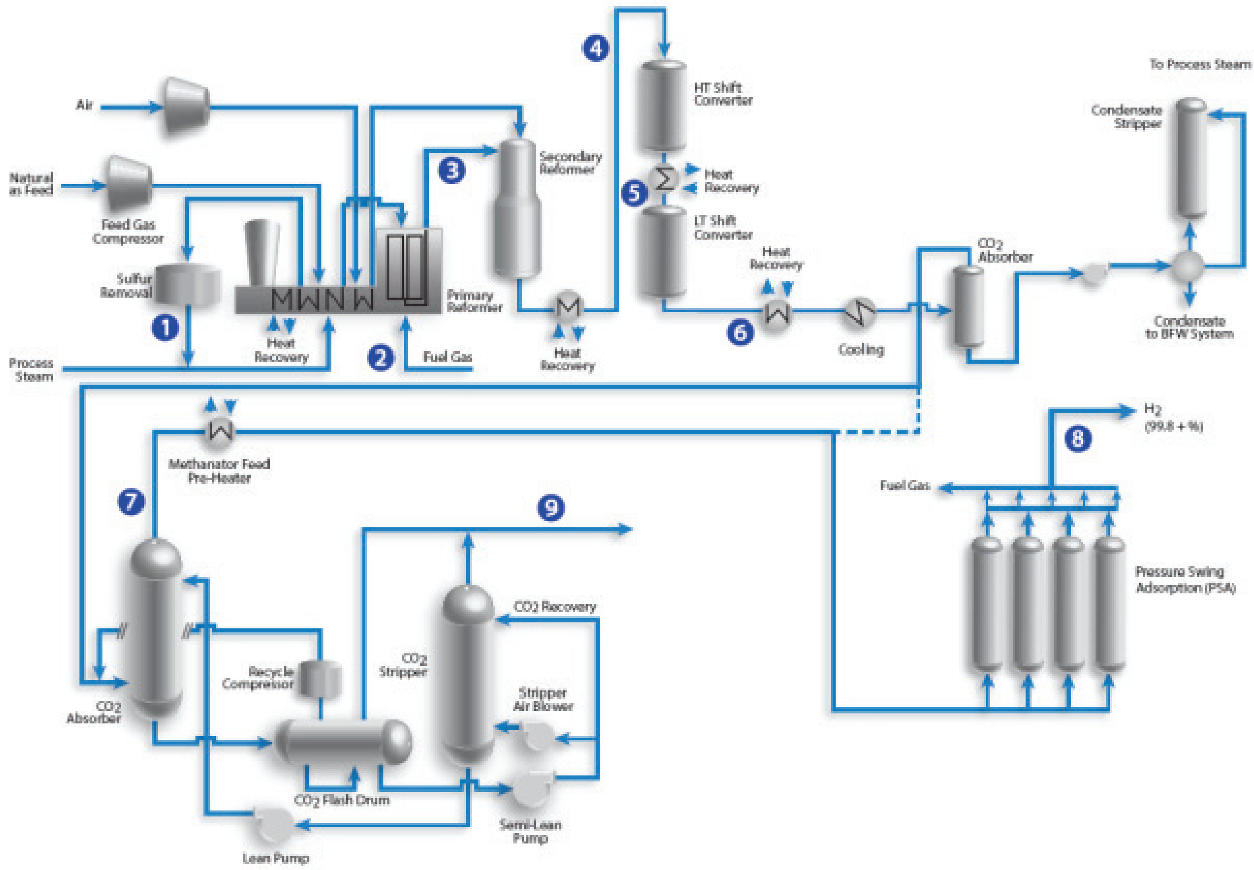

Figure 6. A simplified process diagram for a captive hydrogen plant based on SMR

Table 3. Description of the measurement points in the captive hydrogen plant in figure 6

Measurement Point	Process Description	Key Measurement Parameters
1	Natural Gas Feed to Primary Reformer	Carbon Number
2	Fuel Gas to Reformer Furnaces	BTU
3	Raw Syngas – Primary Reformer Outlet	Composition, CH_4
4	Raw Syngas – Secondary Reformer Outlet	Composition, CO
5	High Temperature Shift Converter Outlet	Composition, CO
6	Low Temperature Shift Converter Outlet	Composition, CO_2
7	CO_2 Absorber Outlet – Feed to PSA	Composition, CO_2
8	PSA Unit H_2 Stream	Composition, H_2
9	CO_2 Recovery Stream	CH_4 Leakage

Table 4. Example stream composition for PSA unit hydrogen stream

Measurement Point	PSA Unit H2 Stream
Temperature (°F)	120
Pressure (psig)	350
Cycle Time (min)	2-4
Hydrogen (%)	99.0
Methane (%)	0.5
Nitrogen (%)	0.4
Carbon dioxide (%)	0.1

All composition values are in mol percent.

One U.S. West coast refinery has used a variety of technologies to measure H_2 purity at the outlet of the PSA process unit. Initially, the plant used a commercial specific gravity (SG) meter for this measurement. However, due to the non-binary nature and due to trace contaminants in the stream, the SG meter would often produce spurious results. In addition, the process engineer needed both a good hydrogen measurement and details of the contaminants, which this sensor was unable to provide. The site investigated alternative approaches and settled on one based on solid state sensing technology. This analyzer was installed and was found to be very sensitive to pressure and flow, and ultimately was deemed not sufficiently repeatable for their requirements. The site evaluated process gas chromatography (PGC) and optical technologies, focusing on process Raman spectroscopy, since other optical technologies that are commercially available, such as near-infrared (NIR) and mid-infrared (NDIR, FTIR) cannot measure hydrogen, whereas the Raman technique can. The site chose process Raman technology over the PGC systems due to the high cost of maintenance and consumables they had experienced with previous PGC installations at the site. Please refer to Table IV for an example PSA hydrogen stream composition.

Some key differences with other process analyzers

The use of optical analyzers, and, in particular, the process Raman analyzer described in this paper, provides some installation and safety benefits over some more conventional process analyzer technologies used for gas composition measurements. Some of these benefits include:

- The analytical sensor can be located at the sample tap. This eliminates the need to transfer the sample from a probe to the analyzer along heat-traced sample lines. This can reduce installation costs, maintenance costs, and can significantly reduce lag time often caused by sample transport.
- Not transporting process sample to the analyzer can improve safety for plant personnel, as no toxic gases are present at or near the analyzer during maintenance activities.
- Gas sample continuously flows past the optical sensor during the analysis period, providing an average composition value. Process analyzers based on separation techniques take a grab sample at a fixed point in time and can take several minutes to provide a result. Changes in the process stream during this time are not captured until the next grab sample is taken.
- Process Raman spectrometers are able to analyze multiple gas streams in parallel, without the need for stream switching.
- The analytical sensor is designed to operate at line temperature and pressure, which provides the plant an opportunity to return the sample to the process and avoid flaring.
- There is an optical service kit available to clean, polish, and repair the fiber optic cable. This kit includes a fault locator tool, a power meter, and a fiber inspection microscope, along with fiber coupling gel and polishing discs, all included in a handy pelican case.

Conclusions

Process Raman Spectroscopy is an analytical method for gas-phase measurements at manufacturing facilities like refineries and fertilizer plants. The inability of other common optical spectroscopic techniques such as NIR and IR to detect homonuclear diatomics such as hydrogen and nitrogen make Raman spectroscopy a uniquely suited optical technique for the analysis of syngas and hydrogen streams that are found throughout these facilities. The successful installations at the facilities described herein provides supporting evidence that process Raman spectroscopy is providing essential data and performance benefits to the monitoring and control of key process units within these plants. The speed of response is extremely important in these changing processes, as refiners look for more feed-forward strategies to fine-tune hydrogen production and lengthen catalyst life and ammonia manufacturers look for energy savings.

Acknowledgments

We want to thank the people at the Coffeyville Resources Nitrogen Fertilizers LLC facility, and specifically Travis Miller, for providing the image for Figure 1, the data for Table I, and support information for the use of process Raman spectroscopy in their plant. I would also like to thank the people at the two West coast refineries (who asked not to be specifically named) for providing us information on the use and benefits of process Raman spectroscopy at their facilities.

Appendix: Raman spectroscopy technology review

Process Raman analyzers are based on inelastic light scattering resulting from directing laser light into a sample. When light interacts with a chemical, it can be absorbed, transmitted, or scattered. Most of scattered light is Rayleigh, or elastic, scattering. A small fraction of scattered photons undergo inelastic, or Raman scattering, losing some energy to vibrational modes of the molecules in the sample. Raman scattered photons have a different wavelength than the incident light. Each type of chemical bond will scatter a different energy, or color, of light, due to the energy states of the chemical bonds between the atoms.

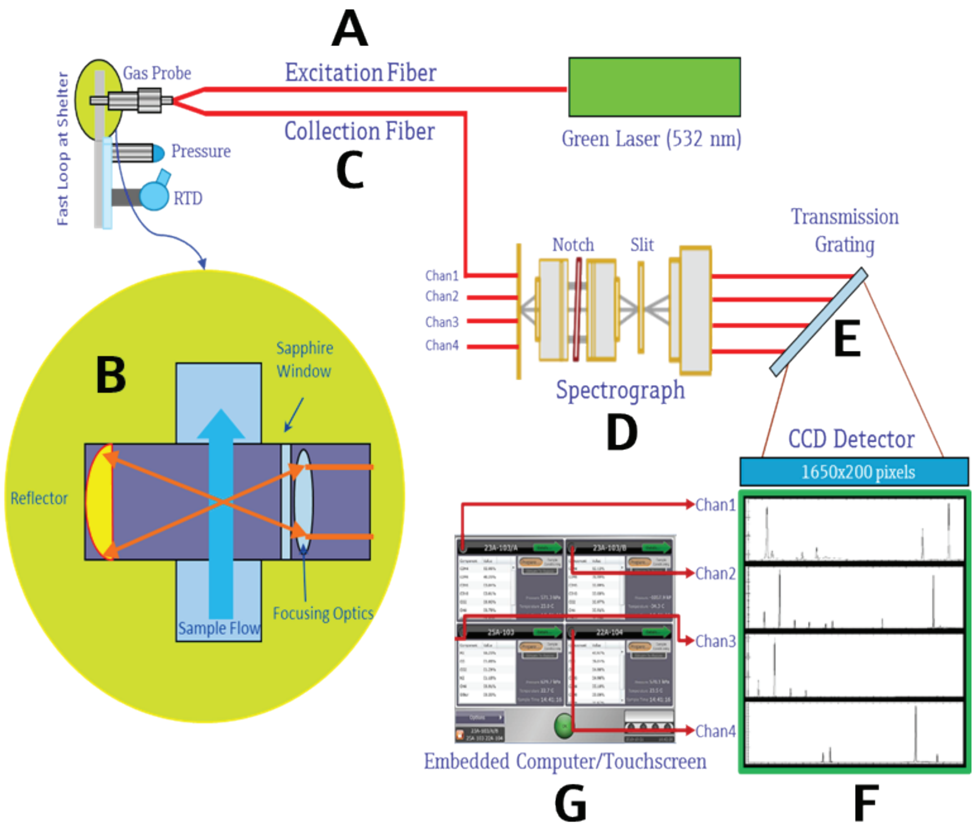

Figure 7. Components of the process Raman analyzer

When Raman spectroscopy is used to measure a gas mixture, each of the different component gases scatters a different color of light. If this light is collected and analyzed, the different colors can be used to identify the components of the mixture, and the intensity of each color can be used to quantify each component in the mixture, providing compositional analysis.

Figure 7 shows the major components of the process Raman analyzer. Laser light is transmitted via a fiber optic cable (A) to the gas probe (B). Scattered light is transmitted along a collection fiber (C) to the spectrograph (D), where Rayleigh scattered light is removed and the Raman scattered light is diffracted via a holographic transmission grating (E) to spatially separate the different colors. The dispersed light is imaged onto a charge-coupled device (CCD) detector (F). Up to four collection fibers from different process streams can be imaged simultaneously onto the CCD, with compositional results and other pertinent information displayed on the graphical user interface (GUI) of the system (G).

Figure 8 illustrates the complete process Raman analyzer solution. The base unit of the analyzer contains all power, the control computer, the Ethernet and RS485 interfaces to the plant DCS, the touch screen display for the GUI, and laser safety features. Each process stream requires an application kit, which consists of a laser, fiber optic cable of appropriate length to reach the sample tap point for that stream, an AirHead™ gas probe, and a software method. The software method, which is unique to the stream being analyzed, is used to convert the collected Raman data into composition data. The solution also includes one of several different sample interfaces for the Raman optical probe to the process sample tap. These interfaces can also provide full sample conditioning, including sample cooling, pressure reduction, water and particulate removal (via a dynamic reflux sampler), and a return stream so that analyzed sample can be returned to the process at a lower pressure point, typically downstream of the sample tap.

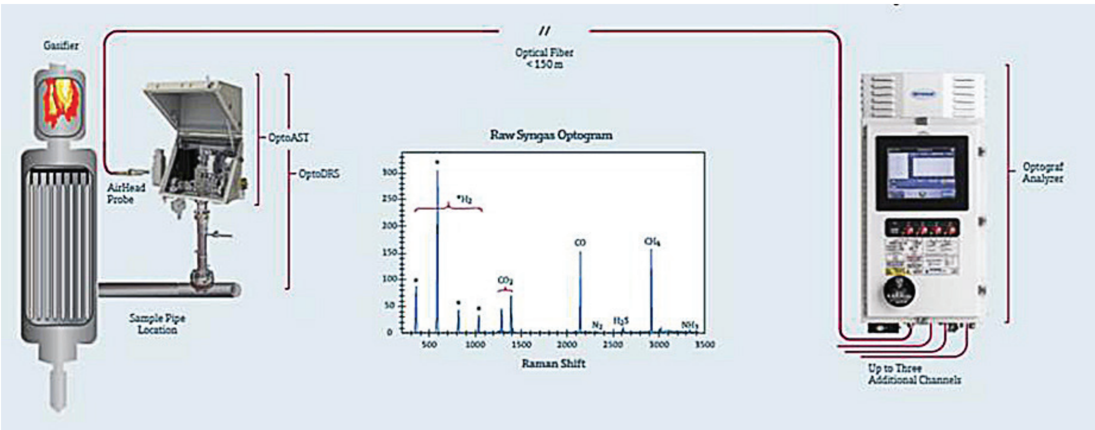

Figure 8. Typical layout of key components of the process Raman spectrometer for measuring of syngas at the outlet of a gasifier

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