Vapor Recovery

Organic components (VOCs) from any location or plant where petroleum products are produced, stored, distributed or handled is increasingly gaining momentum versus combustion of these vapors. At the same time monitoring of other components is an important issue both for emission control and process optimization purposes.

Basically, Vapor Recovery is the process of recovering the vapors; the systems or plants which perform vapor recovery are called Vapor Recovery Units (VRU).

The multiple aims of a VRU are

• to safely prevent harmful volatile organic compounds (VOCs, see text box on page 3) from being released into the atmosphere and/or from generating noxious and potentially explosive fumes and environmental damages and
• to recover gas vapors that can then be made into a usable and profitable product, and
• to enable plant operators or owners to meet legal emission standards in the exhaust gas stream

Involved products and plants

Typical hydrocarbon products involved in the Vapor Recovery issue are gasoline, diesel, jet fuel, naphta, ethanol, methanol, chemicals, solvents, crude oil, alcohols etc.

Plants involved are crude oil tank farms, tanker loading terminals, petroleum distribution terminals, chemical and petrochemical plants, pipeline compressor stations and many more.

Benefits of VRUs

Economic and environmental benefits arise from operating VRU plants:

• Capture of up to 95 percent of hydrocarbon vapors for further use on site or for sale
• Recovered vapors have higher BTU content than pipeline quality natural gas
• Capture of HAPs (Hazardous Air Pollutions) and potential green house gases
Diversity of vapor recovery processes

Vapor Recovery Systems are based on different processing principles. Processes use adsorption, absorption, condensation and membrane separation principles to recover hydrocarbons from vapors and to clean the exhaust gas stream to a level that complies with emission limits.

Activated Carbon Adsorption

VRUs use two scrubbers which are operated in parallel both filled with activated coal. One adsorbs the hydrocarbons and then, once saturated, the scrubbers switch and the hydrocarbons are removed and returned to liquid form.

Refrigeration Condensation

VRUs use a process where the vapor is chilled to a temperature where the hydrocarbons condense out of the vapor stream. Refrigeration fluids cool a heat transfer fluid. This fluid is circulated through the tubes to provide cooling for the condensers.

Lean Oil Absorption

VRUs use a process where the lean oil is forced to intimate contact with the hydrocarbon contaminated air stream in a column (scrubber). The vapor rises through the column in counter flow to the liquid coming down the column. The hydrocarbons are absorbed by the liquid stream, enriched through recirculation and finally flashed out.

Fig. 1 shows, as example, a lean oil absorption process with typical measuring locations for process analyzers at the inlet and the outlet of the process. This may be more or less considered as generic example for use of process analytics in VRUs in general.

The Lean Oil Absorption Process

1. A liquid ring compressor takes the vapor/air mixture from a tank farm and mixes it with the recycle stream from the membrane unit. The mixture is compressed while using a part of the absorbent stream as “liquid hydrocarbon seal” to remove the heat of compression from the gas stream.
2. The mixture is fed to a scrubber column, where the vapor gets in contact with an absorbent flow from the top of the column. The liquefaction of the vapors is effected by condensation and absorption effects.
3. The non-liquefied vapor stream leaves the column at the top and enters another separation stage (e.g. a membrane unit) for further cleaning before being released to the atmosphere.
4. A vacuum pump recycles the separated enriched hydrocarbon stream to the compressor inlet.
5. The clean gas is released into the atmosphere (Source: The BORSIG solution)

The general task of using process analyzers in VRUs is to ensure a reliable, efficient and safe operation of the plant, in detail

- to monitor and control the effectiveness of the VRU in removing the hydrocarbons
- to increase the safety in the area around the VRU by monitoring explosive gas mixtures
- to monitor the exhaust gas stream for gas components which are limited due to environmental regulations.

Typical measuring locations with high priority (inlet and outlet, fig. 1, dark green) or lower priority (light green) are indicated but may be considered as generic information only.

Fig. 1 VRU process flow chart (lean oil absorption principle) with typical measuring locations
In Vapor Recovery Units, Process Analytics play an important role in monitoring and controlling the process. They provide data about the chemical composition of the feed, the recycled product and the exhaust gas which is finally emitted to the atmosphere. This information helps to operate the plant reliably and efficiently, to minimize potential risks and to meet environmental emission limits.

Process analyzers for use in VRUs are preferably Process Gas Chromatographs (PGC) and Continuous Gas Analyzers (CGA).

Process Gas Chromatography (PGC) has been used for decades in the chemical and petrochemical industry. Typically, a PGC will run for multiple component analyses of various hydrocarbons (from low boiling point up to high boiling fractions) but also inert gases such as hydrogen or for key components such as benzene.

Siemens offers the MAXUM edition II PGC which represents the top technology in process gas chromatography for analyzing liquids and vapor process samples. Unparalleled product features deliver high versatility and the best possible analytical results at the lowest cost.

VOCs are a group of hydrocarbons with high volatility. They as well occur naturally as are produced and used in many industrial processes of the oil & gas, chemical and petrochemical industry. Typical VOC sources are crude oil, solvents, fuels, additives, alcohols etc.

VOC emissions, caused by evaporation and other processes, can result in significant health risks. They are also known as precursor substances for ozone gas contributing to global warming. Therefore suitable measures must be taken to minimize VOC emissions.

Regulations have been implemented in many countries to minimize VOC emissions by reduction of VOC consumption and installation of emission control systems.

For VRU especially apply the following regulations:

- **Europe:** 94/63/EC, Directive on the control of volatile organic compound (VOC) emissions resulting from the storage of petrol and its distribution from terminals to service stations.
- **Germany:** Parts of TA Luft and BISchG
- **USA:** Parts of Clean Air Act and EPA regulations
Improved Monitoring of Benzene Recovery Units by Process Chromatography

To monitor the exhaust gas from VRUs before entering the stack is a typical application example for use of gas chromatography. The aim is to analyze the composition of the gas and therefrom to judge whether the process runs properly and the emitted gas complies with the emission limits. Fig. 4 shows a list of gas components with concentration levels which are common in VRUs exhaust gas after processing to recovery benzene vapor as a typical example. Other applications are to determine various hydrocarbon mixtures (e.g. C\textsubscript{1} to C\textsubscript{5} including aromatics) in the raw and the clean gas from mid ppm (raw gas) down to low ppm (clean gas) levels.

Top technology ensures optimal process control

Siemens PGC represent the top technology by providing analyzers that are reliable and robust as well as flexible to meet specific user requirements in terms of installation, applications and analytical performance. Specifically these are for VRU related applications:

- Multiple analytical tools such as injectors, ovens, detectors or columns to adapt the hardware perfectly to the analytical needs
- Accurate determination of all hazardous air pollutants due to perfect adaption of the analytical hardware such as injectors, separation columns and detectors (fig. 5 and 6)
- Precise and interference-free measurement of key components such as benzene or other solvents and chemicals by optimized selection of most suitable separation column sets and column switching technologies
- Precise and sensitive measurement of key components by using selective trace detectors such as flame ionization (FID), flame photometric (FPD) or Pulse Discharge Detectors (PDD)
- Cost effective VRU solutions by using single and independent dual oven GCs for minimizing the number of analyzers
- Reduction of utility costs of the VRU analyzer equipment by airless oven and modular oven technology.

Fig. 5 shows the most frequently used detectors in process gas chromatography. For VRU applications specifically the FID is often used. This detector is highly selective for hydrocarbons which represents a highest number of applications to recover potential air pollutants from storage or loading facilities as well as other typical plants. The Siemens FID detector geometry and gas supply (including air as make up gas) are special designed so that the sensitivity and structural linearity are optimal. In addition this reduces also band broadening of the component signals (peaks) at the detector.

<table>
<thead>
<tr>
<th>Exhaust Gas Components</th>
<th>Concentrations</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min.</td>
<td>Normal</td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Sum C\textsubscript{1}-C\textsubscript{10} Non-Aromatics</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Sum Aromatics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>78.8</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>20.8</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}-C\textsubscript{4} Olefins</td>
<td>&lt; 20</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}-C\textsubscript{4} Saturates</td>
<td>&lt; 20</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>&lt; 5</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>&lt; 5</td>
<td></td>
</tr>
<tr>
<td>Xylenes</td>
<td>&lt; 5</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{5}-C\textsubscript{8} Hydrocarbons</td>
<td>&lt; 5</td>
<td></td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>&lt; 1</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4  Typical measuring task for a benzene recovery unit

<table>
<thead>
<tr>
<th>Detector Type</th>
<th>Selectivity</th>
<th>Typical Detection Limit</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCD, Thermal Conductivity Detector</td>
<td>Universal</td>
<td>1 ... 10 ppm</td>
<td>Main and secondary components</td>
</tr>
<tr>
<td>FID, Flame Ionization Detector</td>
<td>Hydrocarbons</td>
<td>10 ... 100 ppb</td>
<td>Trace hydrocarbons with methanator: CO, CO\textsubscript{2}</td>
</tr>
<tr>
<td>FPD, Flame Photometer Detector</td>
<td>Sulfur and phosphor containing molecules</td>
<td>10 ... 100 ppb</td>
<td>Traces of sulfur components in hydrocarbon matrices</td>
</tr>
<tr>
<td>PDHID, PD Helium Ionization Detector</td>
<td>Universal</td>
<td>5 ... 50 ppb</td>
<td>Trace analysis in highly pure gases</td>
</tr>
<tr>
<td>PDECD, PD Electron Capture Detector</td>
<td>Molecules with electro-negative groups</td>
<td>0.1 ... 1 ppb</td>
<td>Traces of halogenated substances</td>
</tr>
<tr>
<td>PDPID, PD Photo Ionization Detector</td>
<td>Easy ionizable molecules</td>
<td>100 ... 1000 ppb</td>
<td>Aromatic traces</td>
</tr>
</tbody>
</table>

Fig. 5  Detector types in process GC (PD: Pulsed Discharge)

Fig. 6  Flame Ionization Detector combined with a capillary columns set in an airless oven
Siemens Gas Chromatographs - Latest Innovations

Gas Chromatograph Portal Workstation Software

The MAXUM (and MicroSAM) process gas chromatograph product line is supported by the Gas Chromatograph Portal workstation software to more easily monitor and modify MAXUM (and MicroSAM) GCs on an Ethernet network.

The new software upgrades the former System Manager and EZ-Chrom software packages which now have been completely integrated and refined into a new single software package. The new software is fully compatible with existing MAXUM and MicroSAM GCs in the field.

The Gas Chromatograph Portal software resides on a PC workstation (fig. 7) and gives the user the real-time status for all the gas chromatographs on the network. In the event of an alarm, interrogating the analyzer is as simple as clicking on the icon for the analyzer, automatically calling up intuitive screens with all the analyzer’s key performance parameters displayed.

With the Gas Chromatograph Portal, every GC on the network is continually updated to reflect the current analysis and operating status. Analysis results, chromatograms and alarm logs are just a simple click away. Furthermore, automatic data logging and reporting functions are completely supported and each display takes full advantage of the latest user interface features.

Color Touch Screen Maintenance Panel

The newest addition to the MAXUM gas chromatograph (GC) features is now a large color touch screen maintenance display that blends the best features of the previous menu-driven design with icons and graphical elements for simple access to all the standard maintenance features of the MAXUM.

Whether you are a new analyzer technician or a GC veteran, the new display of the MAXUM is the ideal user interface. All the routine gas chromatograph operation and maintenance functions are accessible with a simple touch of the 10-inch color display. Further simplifying access to the MAXUM GC, the touch screen display is fully certified for direct use in hazardous Div. I and Zone 1 areas.

Thanks to the MAXUM GCs open design structure, it is easy to add this color maintenance panel to existing MAXUM GCs by simply exchanging the door of the GC’s electronics section. This is part of Siemens Process Analytics’ commitment to enhancing the product while protecting our customer’s investment in their MAXUM GC system.

Modular Oven

An addition to the regular oven variants (airless, airbath and temperature programmable oven) another option is available using the Modular Oven (fig. 8). This oven option is an airless oven design where complete chromatograph modules are snapped into place. Removal and replacement of a module can be performed in mere minutes, dramatically lowering operation and maintenance of the gas chromatograph. The module can then be repaired at the user’s convenience in their maintenance shop or returned for refurbishment at Siemens. And, as part of the MAXUM GC analysis platform, the modular configuration is completely compatible with any MAXUM system for data communication and reporting.

This oven option is part of Siemens Process Analytics’ commitment to the MAXUM GC platform as the ideal solution for process analysis for years to come.

Fig. 7 Gas Chromatograph Portal workstation software

Fig. 8 MAXUM modular oven with color touch screen
Continuous Gas Analyzers in VRUs

Continuous Gas Analyzers (CGA) are used to continuously determine one or more gas components in process and exhaust gases from various sources. CGAs are extremely versatile: they enable to optimize processes in chemical and petrochemical plants and many other industries; they are indispensable parts of continuous emission monitoring systems (CEMS) and ensure safe operation of plants by monitoring explosive or toxic substances.

In VRUs, the objective for using continuous gas analyzers are:

- **Process control**
  - to run the process under optimal conditions
- **Safety measurements**
  - for protection against explosion
- **Continuous emission monitoring**
  - to comply with legal requirements regarding limits of hazardous components emitted to the atmosphere

Details in using CGAs in Vapor Recovery Units depend strongly on type and size of the plant and on local requirements and regulations. Typical sampling locations are at the inlet and outlet (vent, stack) of the plant and also at locations directly in the process to control process details. Measurement must meet explosion protection relevant requirements (e.g. according European ATEX or North American CSA) at certain locations of the plant.

Typical measuring components are TOC, NMTOC (Non-Methane), Methane, Ethane and Ethene and Oxygen; other components may be required due to special process conditions or local emission control targets. For CEM systems legal requirements have to be observed. In Europe CEMS must be approved acc. to standard EN 15267-3. Once installed, CEMS must comply with EN 14181 (Quality Assurance Levels). In USA and other countries Environment Protection Agency established standards being part of Code of Federal Regulations – for emission monitoring 40CFR60 and 40CRF75 regulations are most important.

Siemens line of CGAs (Overview)

Siemens Process Analytics offers a complete line of continuous gas analyzers which meets all demands of a VRU project (process control and CEM):

**ULTRAMAT 23**

Four channel multicomponent extractive gas analyzer featuring NDIR technology to determine up to three IR active components and electrochemical cell technology for O₂ measurements (O₂ with paramagnetic cell is also possible).

**Series 6**

of high performance extractive gas analyzers for use in Ex or non-Ex areas comprises:

- NDIR-based ULTRAMAT 6 to determine IR-active components
- Paramagnetic-based OXYMAT 6 to determine oxygen
- Thermal conductivity-based CALOMAT 6 to determine H₂ or rare gases
- Flame ionization-based FIDAMAT 6 to determine the total hydrocarbon content

**SIPROCESS UV600**

Determines simultaneously up to three UV-active gas components such as NO, NO₂, SO₂ or H₂S on low measurement ranges.

**Gasmet CEMS FTIR**

Complete solution for simultaneous analysis of multiple gas components i.e.: CO, CO₂, HCl, HF to CH₄, C₂H₆, C₂H₄, C₃H₆, C₆H₁₄, HCOH and many others using Fourier Transform Infrared absorption and hot sampling system.

**LDS 6**

Tunable Diode Laser analyzer to measure O₂, NH₃, HCl, HF, H₂O, CO, CO₂, ... with up to three in-situ cross-duct sensors. Available also in intrinsically-safe version for Ex Zone 0.

**SITRANS SL**

Similar to LDS 6 but in a highly integrated design without fiber-optic cables and with only one pair of cross-duct sensors – a transmitter unit and a detector unit. SITRANS SL determines O₂ and CO.

**SET CEM**

Complete gas analysis system for Continuous Emission Monitoring including sampling probe and sample conditioning system.

SET CEM determines the concentrations of CO, CO₂, NO, NOₓ, SO₂, O₂, HCl, HF, NH₃ and H₂O.
Siemens Process Analytics at a glance

Leading in process analytics

Siemens is a leading provider of process chromatographs, process analyzers and process analysis systems and solutions. We offer our global customers the best solutions for their applications based on innovative analysis technologies, customized system engineering, sound knowledge of customer applications and professional support. From applications in the chemical and petrochemical industry to emission monitoring in waste incinerators and power plants, the highly accurate and reliable Siemens analyzers and chromatographs are the perfect solution for the job.

The chromatographs and analyzers are easily integrated into the Totally Integrated Automation (TIA) concept making Siemens Process Analytics your qualified partner for efficient solutions that integrate process analyzers into automation systems.

Global presence

The global presence of the Siemens service organization permits optimum support for our customers through fast response times onsite. Furthermore, our service specialists are acquainted with the local and regional requirements, standards and directives.

We can offer our customers tailored service products based on our specific knowledge of the processes involved in the oil & gas, chemical, power, cement and other industries.

Plant life-cycle support

As a result of our large service portfolio we are able to support our customers throughout the complete product life cycle (fig. 10). We already develop cost-efficient and reliable analytical concepts during plant planning. Using customized service contracts and competent service onsite we can help to reduce downtimes while simultaneously ensuring optimum operation of the analytical equipment. Our range of services is extended with technical support from experts over the hotline and a comprehensive selection of on-site training courses for service personnel and operators.

FEED

Front End Engineering and Design (FEED) is part of the planning and engineering phase of a plant construction or modification project and is done after conceptual business planning and prior to detail design. During the FEED phase, best opportunities exist for costs and time savings for the project, as during this phase most of the entire costs are defined and changes have least impact to the project. Siemens Process Analytics holds a unique blend of expertise in analytical technologies, applications and in providing complete analytical solutions to many industries.

Fig. 10 Siemens Process Analytics: Plant life cycle services
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