Synthetic Rubber Plants

Maxum Process Gas Chromatograph measures and optimizes Synthetic Rubber production

Rubber
Rubber is a collective term for macromolecular substances of natural rubber (NR) or synthetic rubber (SR) origin. Natural rubber use dates back to the Mayas but was first recognized as technical material in 1851 by Charles Nelson Goodyear. He presented a new material produced from the milk of rubber trees, which had been treated with sulfur and vulcanized to strengthen the rubber. Years later, the development of alternatives for natural rubber was started for a number of reasons including political ones.

Synthetic Rubber
In 1920, the German Hermann Staudinger succeeded in determining the structure of natural rubber which was key to the subsequent development of synthetic rubber in many countries. In Germany, this was followed by a patent for a synthetic rubber in 1929 and by the first large-scale industrial production beginning in 1939. This product was called Buna, from Butadiene as raw material and Natrium (sodium) as catalyst.

These days, process gas chromatographs are a key part of the standard instrumentation of most production plants for synthetic rubber. These analyzers continuously monitor processing variables such as composition of the process streams and play an essential role in efficient plant operation and product quality.

Siemens Process Analytics is well known worldwide for its excellent process analyzer expertise, application know-how, service support and expertise in engineering and manufacturing turnkey solutions particularly those used for synthetic rubber production.
**Synthetic Rubbers**

Synthetic rubbers are complex chemical compounds formed through the polymerization of monomers. Synthetic rubber production (fig. 1) starts with the refining process of oil, coal or other hydrocarbons with naphtha as one of the desired products. The naphtha is then combined with natural gas to produce monomers. Typical monomers used for production feed material include butadiene, styrene, isoprene, chloroprene, acrylonitrile, ethylene or propylene.

These monomers are then polymerized using catalyst and process steam to form chains of polymers which results in rubber intermediaries. These substances are then processed to their final rubber products by vulcanization.

In integrated plants, naphtha or even the monomers and process steam are delivered as raw materials from other production facilities which are located close to the rubber plant.

The synthetic rubber industry provides a wide variety of synthetic rubbers to reflect the different applications and requirements from the market. Examples include:

- Styrene-Butadiene Rubber (SBR),
- Polybutadiene Rubber (BR)
- Polyisoprene Rubber (IR)
- Butyl Rubber (IIR)
- Nitrile Rubber (NBR)
- Halobutyl Rubber (HIIR)
- Ethylene Propylene Diene Monomer (EPDM)

The use of synthetic rubber is widespread, as the characteristics and properties of these elastomers make them useful in almost all economic sectors — automobiles, civil construction, footwear or plastics — playing an important role in the daily life of society.

The SBR and BR forms of synthetic rubber are the most widely consumed type due to their popular use in the manufacture of tires. According to "International Rubber Study Group", world production of synthetic rubber grew from 12.8 to 13.6 million tons in 2006-2007.

As massive investments were required to develop these different varieties, the production technology was heavily concentrated in long-established global major chemical companies such as BASF, Lanxess (formerly Bayer), DOW, Shell, Exxon, DuPont or major players in the tire industry like Goodyear, Firestone or Michelin. Leading world manufacturers are located in Asia and Europe, followed by Northern America and Russia.
Butyl Rubber (IIR) production

Butyl Rubber is a combination of a copolymer of Isobutylene with Isoprene (Isobutylene Isoprene Rubber, IIR).

Polyisobutylene by itself is fully saturated; therefore, isoprene is added to provide sufficient double bonds to allow vulcanization with sulphur.

An outstanding property of IIR is its very low permeability to air and other gases making it ideal for use as tire inner tubes. Other properties include very good resistance to sunlight, ozone and aging and, when used in tires, reduced rolling resistance and thus reduced vehicle fuel consumption.

Production process

- **Feed blending** (fig. 2, section 1)
  Butyl Rubber typically consists of about 98% Isobutylene with 2% Isoprene distributed randomly in the polymer chain. The most commonly used polymerization process uses methyl chloride as a reaction diluent. Chillers are used to cool the blended feed stream before it enters the reactor.

- **Polymerization and stripping unreacted monomers** (section 2)
  Butyl rubber is produced by co-polymerizing isobutylene with a small amount of isoprene, in a solution with methylchloride and a chilled catalyst. To achieve high molecular weight, the exothermic reaction must be controlled at low temperatures close to -100°C.

  During the reaction, a slurry of fine particles of butyl rubber dispersed in ethyl chloride is formed in the reactor.

  The methyl chloride and unreacted monomers are flashed and stripped overhead in a sequence of distillation columns by the addition of steam and hot water.

- **Recycle compression and purification** (section 3 and 4)
  Solvent and isobutylene are recovered and dried and recycled to the polymerization section, while impurities are purged out.

- **Finishing** (section 5)
  Slurry aids and antioxidants are introduced to the hot water/polymer slurry to stabilize the polymer and prevent agglomeration. Then the polymer is screened from the hot water slurry and dried in a series of extrusion dewatering and drying steps. Fluid bed conveyors are used to cool the product to acceptable packaging temperature.
Using the Maxum Gas Chromatograph (GC) for process optimization

Measurement objective

In production plants that manufacture synthetic rubber material, process gas chromatographs play a key role to control the various process sections. They provide critical data about the composition of the feed, intermediates and the final products. This enables the plant's control system to increase the productivity, reliability and availability of the production plant.

Leading technology ensures optimal process control

Process Gas Chromatography (PGC) has been used for decades in the chemical industry to detect potential plant faults early on and safeguard production availability.

Typically, a PGC performs multiple component analyses of various hydrocarbons (from low boiling point up to high boiling fractions) along with light gas measurement such as hydrogen. Siemens Maxum GC represents the leading technology in process gas chromatography for analyzing liquids and vapor process samples. Unrivaled product features deliver high versatility and the best possible analytical results at the lowest long-term cost.

Multiple analytical tools such as injectors, ovens, detectors and columns are available to perfectly match the hardware to the analytical needs:

- Liquid injection valves to optimize the vaporization of liquid samples
- Broad range of column types and columns switching technologies available to provide dependable results in the shortest analysis time
- Sensitive detectors to detect trace components
- Single and independent dual oven concepts for minimizing the number of analyzers
- Airless oven option to reduce long-term utility costs

Key analytical hardware

A key element in process gas chromatography is the injection of the sample into the analysis system as well as the switching of the separation columns to backflush unmeasured components out of the analytical system.

For standard vapor applications (component concentrations in the percentage level), the Model 50 valve (10-port membrane valve) combines sample injection and column switching into one valve. This simplifies the analytical hardware and reduces maintenance requirements. By using a teflon coated stainless steel diaphragm, the Model 50 is very robust and allows switching cycles up to 10 million operations without maintenance.

In synthetic rubber plants, a significant amount of process samples are in the liquid phase in the process. Therefore, the sample has to be vaporized before it can be analyzed. This makes the injection technology used by the analyzer very important to guarantee that the measurement is accurate and the results are representative of the actual process stream.

Fig. 3 shows an automated liquid injection valve to introduce the liquid into a separately heated vaporization chamber and convert it into the gas phase inside the analyzer. The injection valve is flexible in terms of injection volume, sealing material, sample split ratio after vaporization and even the material of the sample wetted parts. This enables optimum configuration that is tailored to the specific requirements of the sample for a reliable and precise analysis.

Fig. 3: Key analytical hardware for synthetic rubber applications
Left: Model 50 injection & backflush valve,
Center: Double oven with model 50 configuration (left) and valveless configuration (right),
Right: Liquid sample injection valve
C4/C5 hydrocarbon analysis using Analytical Setups

In the core process of synthetic rubber production, monomers are mixed in various proportions to be copolymerized to create synthetic rubber products with a range of physical, chemical and mechanical properties. These monomers, such as 1,3 butadiene (SBR plants), isobutylene and isoprene (IIR plants), are all C4 and C5 hydrocarbons.

To date, gas chromatography based analyzers are widely used for the determination of these constituents due to its high specificity. The analysis of individual C4/C5 species requires GC columns which are specialized in the separation of various C4-isomers. Typically GC columns are used with varying selectivity to increase the overall separation power of the method. The columns are combined with a switching valve that transfers the unseparated portion of the chromatogram eluting from the first column to the second, for final separation can occur. The most frequently used analytical configurations (Setups) are shown in fig. 4.

Combinations of the configurations also allows the integration of multiple applications into one analyzer.

Fig. 4: Analytical Setups (configurations) of the Maxum GCII
**Measurement tasks**

The details of the measurement tasks, sampling locations and concentration values of the components differ from plant to plant according to process type and specific plant designs. But the measured components themselves will be very similar in most cases. Fig. 6 shows a typical list of measured components and references to the flow chart of fig. 2.

Most of the components are determined by gas chromatography, but continuous gas analyzers are also used for applications such as combustion optimization and exhaust gas emission control at different locations of the plant.

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**Maxum GC benefits for plant optimization**

Maxum process gas chromatographs provides a number of unique benefits for plant optimization:

- By offering an broad variety of analytical options, Maxum serves as a single platform that can be configured according to the actual analytical needs and thus provide optimum possible results.
- The Maxum workstation software provides real-time information from all chromatographs on the network for immediate response to any changing situation.
- Maxum features flexible networking options including Modbus/TCP and Ethernet. This allows easy and secure integration into the plant’s control systems.
- Due to its well-proven design and the integrated diagnosis functions, Maxum offers an outstanding availability which is of highest importance in process plant control.

A large and well experienced Siemens team stands behind any application and installation for complete user support, if needed. This ranges from broad application know-how to efficient worldwide service capabilities.

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**Fig. 5: Maxum Color Touch Screen Maintenance Panel**

**Fig. 6: Measurement tasks and measured components**

<table>
<thead>
<tr>
<th>Section</th>
<th>Product stream / Measuring task</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Isobutene-Isoprene fraction to basic charge</td>
<td>n-Butylene, Isobutylene, Amylene, Isoprene</td>
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<tr>
<td></td>
<td>Charge Correct feed composition control</td>
<td>n-Butylene, Isobutylene, Amylene, Isoprene</td>
</tr>
<tr>
<td>2</td>
<td>Polymerization and Degassing Correct polymerization process control</td>
<td>Isobutylene, Methylychloride, Isoprene, n-Butylene, Amylene</td>
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<tr>
<td>3/4</td>
<td>Returnable products processing (1) Correct recycle steps control</td>
<td>Oxynge, Methylychloride, Isobutylene, Amylene, n-Butylene, Amylene</td>
</tr>
<tr>
<td></td>
<td>Returnable products processing (2) Correct recycle steps control</td>
<td>Isobutylene, Isoprene, Methylychloride, n-Butylene, Amylene</td>
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<tr>
<td></td>
<td>Returnable products distilling (1) Correct recycle steps control</td>
<td>Methylychloride, Isobutylene, Amylene</td>
</tr>
<tr>
<td></td>
<td>Returnable products distilling (2) Correct recycle steps control</td>
<td>Nitrogen, Methylychloride</td>
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<tr>
<th>Section</th>
<th>Product stream / Measuring task</th>
<th>Component</th>
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<tbody>
<tr>
<td></td>
<td>Combustion gas (1) Combustion optimization Emission monitoring</td>
<td>CO, NO, O₂</td>
</tr>
<tr>
<td></td>
<td>Combustion gas (2) Combustion optimization Emission monitoring</td>
<td>CO, CH₄, NO, O₂</td>
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<tr>
<td></td>
<td>Mixed isobutene fraction</td>
<td>Isobutane, Isobutene, n-Butane, 1.3-Butadiene, 2-Butylene, C5 - C9 hydrocarbon, C1 - C3 hydrocarbon</td>
</tr>
<tr>
<td></td>
<td>Contact gas</td>
<td>Hydrogen, Methane, C2 hydrocarbon, C3 hydrocarbon, Isobutane, Isobutene, n-Butene, 2-Butylene, 1.3-Butadiene, C5 - C9 hydrocarbon, Carbon Monoxide, Carbon dioxide, Nitrogen, Water</td>
</tr>
</tbody>
</table>
Siemens Gas Chromatographs – Innovations

Gas Chromatograph Portal Workstation Software

The Maxum (and MicroSAM) process gas chromatograph product line uses the Gas Chromatograph Portal workstation software to easily monitor and modify Siemens GCs over an Ethernet network.

The new software replaces the former System Manager and EZ-Chrom software packages with a completely integrated and refined 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 Siemens gas chromatographs on the network. In the event of a maintenance event, 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 modern Windows user interface features.

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 GC’s 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 existing Maxum GC system.

Modular Oven

In addition to the regular oven variants (airless, airbath and temperature programmable oven), a new Modular Oven (fig. 8) is available. 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 oven configuration is completely compatible with any Maxum system for data communication and reporting.

Color Touch Screen Maintenance Panel

The newest feature for the Maxum GC features is a large color touch screen maintenance display (fig. 6) that blends the best features of the previous menu-driven design with icons and graphical elements for simple access to all the standard maintenance functions of the Maxum.
Siemens Process Analytics at a glance

Leading in process analytics

Siemens is a leading provider of process chromatographs, process continuous 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 precise and reliable Siemens analyzers are the ideal solution.

Siemens 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 provides optimum support for our customers through fast on-site response times. Furthermore, our service specialists are acquainted with the local and regional requirements, standards and mandates. 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.

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Fig. 9: Siemens Process Analytics: plant life cycle services

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