Rubber
Rubber is a collective term for macromolecular substances of natural (natural rubber, NR) or synthetic (synthetic rubber, SR) origin. Natural rubber was already used by the Mayas but was recognized as technical material first in 1851 when Charles Nelson Goodyear presented a new material produced from the milk of rubber trees, which has been treated with more or less amounts of sulfur and vulcanized.

Years later, a number of reasons including political events were responsible for the development of alternatives for natural rubber.

Synthetic Rubber
In 1920, the German Hermann Staudinger succeeded in determining the structure of natural rubber which was the 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. The respective product was called Buna, from Butadiene as raw material and Natrium (sodium) as catalyst.

These days, process gas chromatographs are part of the standard instrumentation of most production plants for synthetic rubber. Their objective is to continuously monitor and control processing variables such as composition of the process streams. Measuring results are essential to plant efficiency and product quality.

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

Synthetic rubbers are complex chemical compounds built by means of 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 resulting products. The naphtha is then combined with natural gas to produce monomers. As feed material, typically monomers such as butadiene, styrene, isoprene, chloroprene, acrylonitrile, ethylene or propylene are used.

These are then treated by polymerization using catalyst and process steam to form chains of polymers which finally results in rubber substances.

These substances are then processed to 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 high number of different synthetic rubbers which are produced in chemical plants world wide to reflect the different applications and the wide range of requirements from the market.

Examples are

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

and many more.

The use of rubber is widespread, as the characteristics and properties of these elastomers make them useful in almost all economic sectors such as automobiles, civil construction, footwear or plastics so that they are of crucial importance in the daily life of society.

As they are most widely used to produce tires, the SBR and BR varieties are the most widely consumed type of synthetic rubber.


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 solution copolymer of Isobutylene with some percent of 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.

The outstanding property of IIR is the very low permeability to air and other gases why it is used for tire inner tubes. Other specialities include very good resistance to sunlight, ozone and aging and, when used in tires, reduced rolling resistance and thus reduced fuel consumption for “green mobility”.

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 reaction diluent. Chillers are used to cool the blended feed stream before it is fed to 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. 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 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 aid and antioxidant 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.
Inputs of MAXUM edition II to process optimization

General objective
In production plants to produce synthetic rubber material process gas chromatographs play a dominant role to control various process sections. They provide key data about the composition of the feed, intermediates or the final products. This enables the control system to increase the productivity, reliability and availability of the production plant, to cut maintenance costs and to minimize potential risks.

Top technology ensures optimal process control
Siemens Plant Reliability Solutions aims to detect potential plant faults early on and safeguard availability as well as productivity. Process Gas Chromatography (PGC) has been used for decades in the chemical industry. Typically, a PGC will be running for multiple component analyses of various hydrocarbons (from low boiling point up to high boiling fractions) but also inert gases such as hydrogen. MAXUM edition II 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. These are:

- Multiple analytical tools such as injectors, ovens, detectors or columns to adapt the hardware perfectly to the analytical needs
- Liquid injection modules to optimize the evaporation of liquid samples
- Broad range of column types and columns switching technologies available to provide perfect customized solutions
- Sensitive detectors to determine trace components
- Single and independent dual oven concept for minimizing the number of analyzers
- Airless oven to reduce utility costs

Key analytical devices
A key element in process gas chromatography is the injection to introduce the sample into the system and the switching of the separation columns to recondition the system by backflushing remaining components or to cut components out of the 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 unit. This simplifies the analytical train and reduces maintenance requirements significantly. Due to its design, using a teflon coated stainless steel diaphragm is very robust and allows switching cycles up to 10 million on clean samples without maintenance.

In synthetic rubber plants a significant amount of process samples which has to be extracted out of the process and analyzed by the online gas chromatograph are in the liquid phase due to the used raw materials such as styrene (SBR plants) or liquefied isobutylene (IIR or Nd-PBR plants). Therefore, the sample has to be vaporized before it can be analyzed. This indicates that the injection technology of the analyzer gains in importance to guarantee that the measurement is accurate and the results are representative for the actual process stage.

Fig. 3 shows an automated injection module to introduce the liquid into the separately heated vaporization chamber and convert to the gas phase inside the analyzer. The module equipment is flexible in terms of injection volume, sealing, sample split ratio after vaporization or even the material of sample wetted parts. This guarantees best adjustment according to the requirements of the sample for a reliable and accurate analysis.

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 achieve products with a range of physical, chemical and mechanical properties. The module equipment is flexible in terms of injection volume, sealing, sample split ratio after vaporization or even the material of sample wetted parts. This guarantees best adjustment according to the requirements of the sample for a reliable and accurate analysis. These monomers such as 1.3 butadiene (SBR plants), isobutylene and isoprene (IIR plants) are hydrocarbons C4/C5.
To date, gas chromatography based analyzers are most 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 (fig. 5). Typically GC columns are used with different selectivity to increase the overall separation power of the method. The columns are coupled together with a switching device that transfers an unseparated portion of the chromatogram eluting from the first column to the second, where complete separation can be realized. Most frequently used analytical configurations (Setups) are shown in fig. 4.

Combinations of the configurations allow also densification options to integrate applications into one analyzers instead of using two.

Fig. 5: Separation of C4 isomers
Measuring tasks

Details of measuring tasks, sampling locations and concentration values of the components differ from plant to plant according to process type and specific plant design. But the measuring components themselves will be very similar in all cases. Fig. 7 shows a typical list with reference to the flow chart of fig. 2.

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

MAXUM edition II benefits for plant optimization

MAXUM edition II process gas chromatograph provides a number of extensive benefits for plant optimization:

- Offering an outstanding broad variety of analytical possibilities and a consequent modular design, MAXUM edition II can always be configured according to the actual analytical needs and thus provide best possible results.
- The new software portal provides real-time information from all chromatographs and allows continuous control and immediate reaction to any changing situation.
- MAXUM edition II features variable networking possibilities including Modbus/TCP and Ethernet. This allows easy integration into plant automation systems.
- Due to its well-proven and multiple tested design and the integrated diagnosis functions, MAXUM edition II offers an outstanding availability which is of highest importance in process plant control.

A large and well experienced team stands behind any application and installation to provide any kind of user support, if requested. This ranges from broad application know how to efficient world wide service capabilities.

<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>Correct feed composition control</td>
<td></td>
</tr>
<tr>
<td>Charge</td>
<td>Correct feed composition control</td>
<td>n-Butylene, Isobutylene, Amylene, Isoprene, Methylchloride</td>
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<tr>
<td>2</td>
<td>Polymerization and Degassing</td>
<td>Isobutylene, Methylchloride, Isoprene, n-Butylene, Amylene</td>
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<tr>
<td></td>
<td>Correct polymerization process control</td>
<td></td>
</tr>
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<td>3/4</td>
<td>Returnable products processing (1)</td>
<td>Oxygen, Methylchloride, Isobutylene, Isoprene, n-Butylene, Amylene</td>
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<tr>
<td></td>
<td>Correct recycle steps control</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Returnable products processing (2)</td>
<td>Isobutylene, Isoprene, Methylchloride, n-Butylene, Amylene</td>
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<tr>
<td></td>
<td>Correct recycle steps control</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Returnable products distilling (1)</td>
<td>Methylchloride, Isobutylene</td>
</tr>
<tr>
<td></td>
<td>Correct recycle steps control</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Returnable products distilling (2)</td>
<td>Nitrogen, Methylchloride</td>
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<td></td>
<td>Correct recycle steps control</td>
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<td></td>
<td>Mixed isobutene fraction</td>
<td>Cobalt, Iron, Carbon, Hydrogen, Carbon monoxide</td>
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<td></td>
<td>Combustion gas (1)</td>
<td>CO, NO, O₂</td>
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<td></td>
<td>Combustion optimization</td>
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<tr>
<td></td>
<td>Emission monitoring</td>
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<tr>
<td></td>
<td>Combustion gas (2)</td>
<td>CO, CH₄, NO, O₂</td>
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<td></td>
<td>Combustion optimization</td>
<td></td>
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<tr>
<td></td>
<td>Emission monitoring</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Contact gas</td>
<td>Hydrogen, Oxygen, Carbon, Carbon monoxide, Water, Nitrogen, Methylchloride</td>
</tr>
</tbody>
</table>

Fig. 6: MAXUM - Color Touch Screen Maintenance Panel

Fig. 7: Measuring tasks and measuring components
Siemens Gas Chromatographs – 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. 8) 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.

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 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. 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.

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.
**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 will always do a perfect 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.

![Diagram of Siemens Process Analytics: Plant life cycle services](image-url)

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