SIEMENS

Process Analytics

Use of Process Analytics in TDI plants

Process Gas Chromatographs and Gas Analyzers from Siemens are part of automation in TDI plants

TDI and its wide-spread use

TDI (toluene diisocyanate) is one of the most important intermediates of the plastics industry with increasing market demand worldwide. Driving force is the increasing need for polyurethanes (PUR), a multiple applicable class of plastic materials which are produced from TDI (and MDI, methylene diphenyl diisocyanate) as well. Consequently, new TDI production plants are under construction and/or will be constructed in the future, which include substantial measuring and process analytical field instrumentation.

Growing demand for PUR

PUR is needed to produce long-resting and versatile applicable foams. These are used as insulants in buildings or refrigerators, for cushioning of mattrasses, furniture or cars, to construct bodywork, as adhesives or coatings or to produce sport or leisure articles. This identifies global issues such as energy efficiency or climate change as well as mobility and sport acting as general drivers of this fast increasing PUR and TDI demand.

Production of TDI

Various TDI production processes (routes) have been developed by chemical companies such as e. g. BASF AG or BAYER AG. An example is the new plant of BASF in Ludwigshafen which will be put into operation in the near future. Both the following process description and fig. 1 refer to this plant (Source: BASF-Brochure "TDI für Europa", 2012).

TDI is produced (fig. 1) in three steps from nitric acid, toluene, hydrogen, carbon monoxide and chlorine. First, nitric acid reacts with toluene to form Dinitrotoluene (DNT), which, in the second step, is catalyzed with hydrogen to Toluene Diamine (TDA). In the third step, TDA reacts with phosgene to form TDI. Phosgene is not added as such but is formed in the process itself from its source materials CO and Cl. Finally, TDI is cleaned by distillation. HCl is produced as byproduct, recycled and returned to the process.

The final product (Polyurethane foam) is formed by the reaction of TDI with so called Graft Polyoles. These are dispersions of plastic particles which provide stability, elasticity and hardness to the foam material.

The raw materials of TDI are usually available as products or byproducts from other plants at large locations of big chemical companies. So, a TDI plant is often integrated in an already existing plant network.

Siemens Process Analytics involved

Process Analyzer are an important part of field instrumentation in TDI plants. Siemens Process Analytics contributes to this challenging application with its high performance Process Gas Chromatographs and Continuous Gas Analyzers.

Process Analytics in TDI plants

TDI plants are equipped with comprehensive measuring and control instrumentation in order to comply with the strict requirements of quality, safety, environmental and energy efficiency control. Field instrumentation includes process analyzers and analyzer systems to monitor in detail the production steps by analyzing the mass flow streams for their composition und communicate the measured data to the central control system. For that, Siemens Process Analytics offers well proven analyzer (gas chromatographs and continuous gas analyzers) as well as analyzer systems together with specific application knowledge

Measuring tasks in TDI plants

Fig. 1 shows the flow chart of a TDI plant including typical measuring points (1-5) for process analytics.
Table 1 displays corresponding details including application, measuring components, concentration ranges and suitable Siemens analyzers.

In a separate plant area, chlorine is produced and recycled; related measuring points are in summary marked with 6. Fig. 2 and table 2 show details without addressing exact locations in the plant.

Sampling point and application	Measured component	Concentration range	Siemens Analyzer
1 Purity/ Quality of H_2	H_2	98 ... 100 %	MAXUM Ed. II Process Gas-Chromatograph
	CH_4	Low ppm range	
	CO		
	CO_2		
	N_2/Ar	0 ... 1 Mol %	
2 Purity/ Quality of CO	CO	90 ... 100 %	MAXUM Ed. II Process Gas-Chromatograph
	CH_4	0 ... 1 %	
	H_2		
	CO_2		
	N_2/Ar		
3 Safety, Environment	Phosgene	Low ppm range	MAXUM Ed. II Process Gas-Chromatograph
	MCB (Mono-chlorobenzene) in N_2/CO		
4 HCl in process pipe	MCB	Low ppm range	MAXUM Ed. II Process Gas-Chromatograph
	ODB (Orthodi-chlorobenzene)		
	CO	Middle ppm range	
	CO_2	Low % range	
	H_2		
	N_2		
5 Monitoring the Graft plant for leakages	Acrylnitrile	ppm range	MAXUM Ed. II Process Gas-Chromatograph
	Styrene		
6 Chlorine plant	See separate table		

Table 1: Details of gas analysis (ref. Fig. 1)

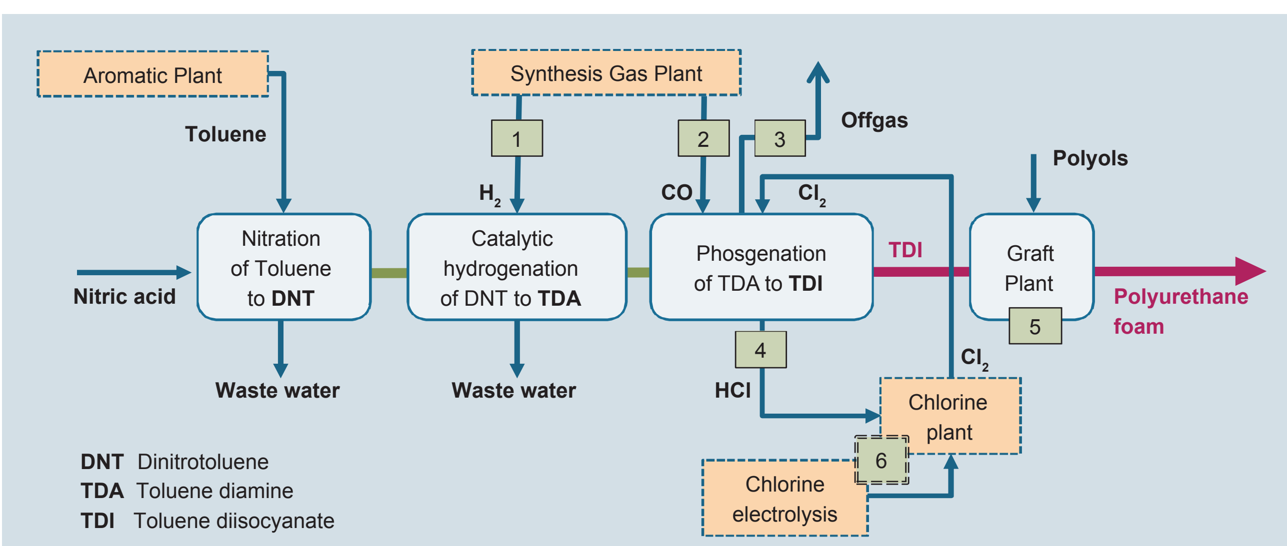

Fig. 1: TDI production flow chart

Chlorine-alkali electrolysis process

Chlorine is a very important substance in chemical industry to produce polymers, resins or elastomers. The chlorine-alkali electrolysis process (diaphragm method, fig. 2) is preferably used to produce chlorine. For quality and safety reasons (hydrogen is involved, danger of explosive gas) the process is monitored at various locations by process gas analyzers. An important requirement is the suitability for operation in aggressive surroundings. Typical applications are listed in table 2.

To reduce the high demand of electricity for this process a recent development by Bayer Material Science has led to the new innovative oxygen depolarized cathode (ODC) technology which modifies the reaction at the cathode: now Oxygen is reduced and no hydrogen produced any more. By this effect the electrode potential is reduced by 30 % appr. and consequently the energy consumption as well.

Application	Measured component	Concentration range	Siemens Analyzer
Monitoring of eletrolysis cell room	H_2	High ppm to low % ranges	MAXUM Ed. II Process Gas-Chromatograph
	N_2		
	O_2		
	CO_2		
	CO_2		
Cl_2 quality monitoring up-/downstream	H_2	Traces	MAXUM Ed. II Process Gas-Chromatograph
	N_2	Traces	
Monitoring of inert gases	O_2	High % ranges	MAXUM Ed. II Process Gas-Chromatograph
	N_2		
	H_2		
	Argon		
Monitoring O_2 in H_2	O_2	Low % ranges	OXYMAT 6
Safety monitoring (workplace)	H_2	Traces	CALOMAT 62/ Electrochem. Sensor
Safety monitoring (workplace)	Cl_2	Traces	Electrochem. Sensor

Table 2: Gas analysis applications in a chlorine-alkali plant

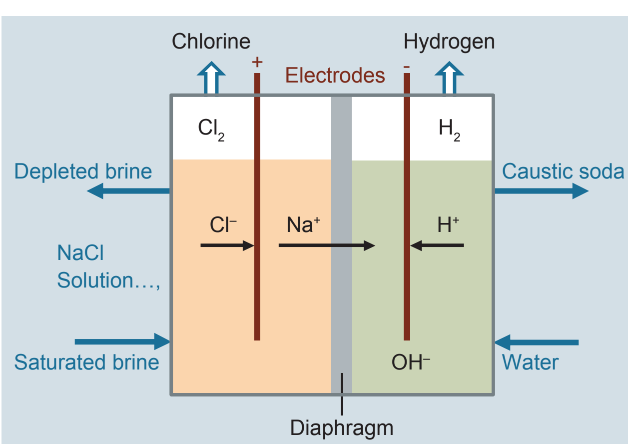

Fig. 2: Chlorine-alkali electrolysis (principle, membrane process)

Fig. 3: Chlorine-alkali production hall

Use of Siemens Process Analyzer in TDI plants

Process Gas Chromatograph (PGC) MAXUM edition II
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 airless dual and modular oven concepts for minimizing the number of analyzers and to reduce utility costs
- Oven with airbath or fan-free airless heating principles
- Optional use of corrosion-resistant materials

The value proposition is based on the customization flexibility to configure the analyzer. This results in a best analyzer performance.

In case of being installed in a network, the new "Gaschromatograph Portal" software provides real time information from all chromatographs and allows continuous control and immediate reaction to any changing situation.

Fig. 4: MAXUM edition II PGC variants

Series 6 Continuous Gas Analyzers
In TDI and the respective chlorine plants also continuous gas analyzers are used to monitor e. g. hydrogen and oxygen. These are CALOMAT 62 and OXYMAT 6 out of the well-proven Series 6 of Siemens Gas Analyzers. Both are available in an IP65 field housing or as 19” rack unit.

CALOMAT 6/62 use a thermal conductivity detector and determine the concentration of e. g. hydrogen, nitrogen or other gases in binary gas mixtures by determining the thermal conductivity of the sample gas. CALOMAT 62 is especially designed for applications in corrosive gases e. g. in the chlorine electrolysis process.

Most frequently used for demanding applications, the **OXYMAT 6** meets high standards with regard to reliability and measuring quality.

The OXYMAT 6 measures oxygen using the paramagnetic alternating pressure method. This guarantees perfect linearity and allows parameterization of minimal and highest measuring ranges of in a single device. The sensor in the detector does not come into contact with the sample gas thus allowing the measurement of corrosive gases.

All series 6 analyzers provide an open interface architecture (RS 232, RS 485, PROFIBUS) and are easily to be integrated into communication networks. For efficient maintenance the analyzer can communicate over TCP/IP using the Siprom GA software tool.

Fig. 5: CALOMAT 62 Gas Analyzer

Conclusion

Driven by the global demand, new TDI plants are constructed or old ones revamped. As part of the field instrumentation, process analyzers are indispensable. Siemens Process Analytics provides proven gas chromatographs and gas analyzer combined with the specific application know-how and long lasting experience in system integration.

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