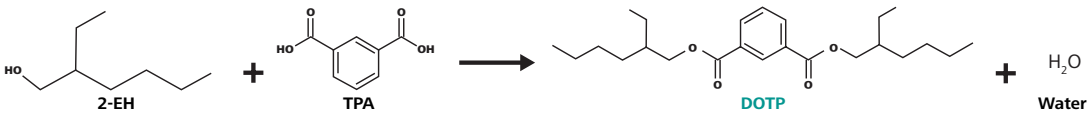
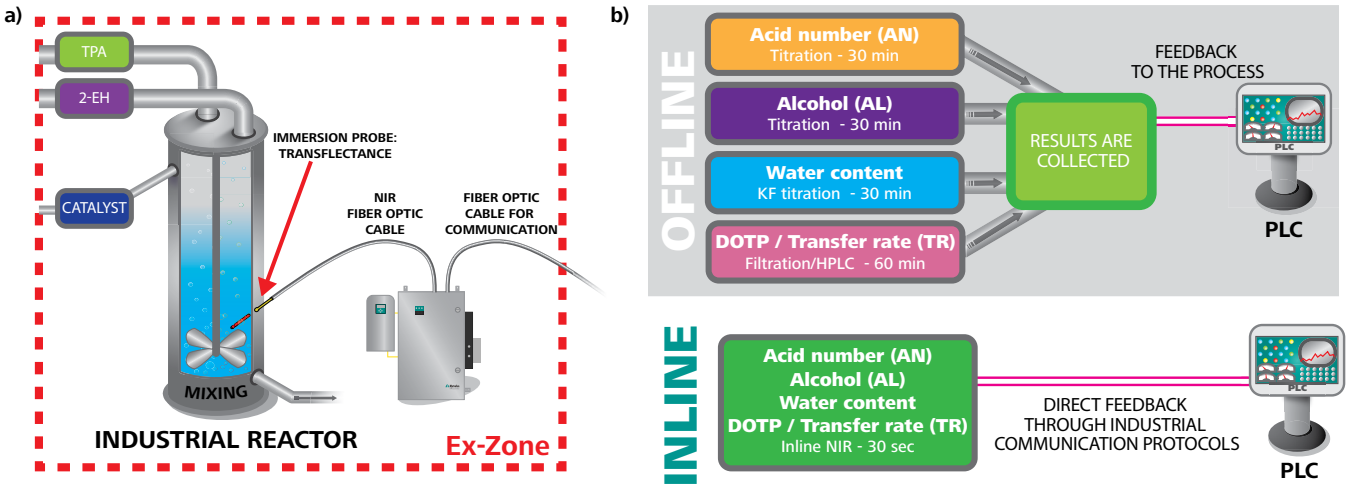
Monitoring of DOTP production via esterification with inline analysis

Polyvinyl chloride (PVC) is a plastic polymer which is seen all over in everyday life – in pipes, bank cards, sports equipment, and even furniture. It is generally rigid, but can be made into more flexible forms with the addition of *plasticizers*. A plasticizer is a liquid or solid additive that can change the physical properties of a material (*e.g.* plastic or elastomer). This occurs because plasticizers are bulky, polar, organic molecules that decrease the intermolecular interactions between the chains of a crystalline polymer, making it more flexible or softer. Phthalate esters (*e.g.* di-2-ethylhexyl phthalate «DEHP» and diisononyl phthalate «DINP») are the main type of plasticizers used to modify PVC, and accounted for 65% of global plasticizer consumption in 2017. However, due to environmental and health risks, the world consumption of phthalate ester plasticizers is expected to decrease by 2022, and non-phthalate plasticizers are expected to take over the market.



Dioctyl terephthalate (DOTP or DEHT), is an organic molecule with the chemical formula $C_6H_4(CO_2C_8H_{17})_2$ and it is a *non-phthalate* plasticizer. This colorless viscous liquid is known to be a great substitute for other harmful phthalates. One of the most common methods for manufacturing DOTP is by direct esterification of purified terephthalic acid (TPA) and the branched-chain 2-ethylhexanol (2-EH). TPA comes in pelleted form, 2-EH as a liquid solution, and they are mixed together in a 1:2 ratio in an industrial reactor. A catalyst is added and the temperature is maintained between 160 and 235 °C for a few hours. During this time, DOTP is formed together with water, which is stripped out to keep the moisture content low over the course of the reaction. High purity DOTP is obtained through this process.



a) Stylization of suggested placement for Near-infrared (NIR) probe in an industrial DOTP reactor. b) Steps to measure important parameters by implementing offline or inline analysis.

Many parameters need to be monitored in order to guarantee high yield of the reaction and high DOTP quality. Traditionally, the amount of reactants and products are measured in the laboratory after taking a sample out of the process. However, manual laboratory methods can give long response times in case of process changes (*e.g.* reaction mixture, moisture levels, …), and sample preparation (dilution, filtration, pipetting…) can introduce errors altering the precision of the analysis. Additionally, it can be quite cumbersome since four different operating procedures need to be implemented to analyze these parameters: the acid number (AN) for TPA, alcohol (AL) for 2-EH, ester for DOTP, and water.

Keywords: PVC, plasticizers, DOTP, NIR, spectroscopy, reaction monitoring, chemical free, XDS

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The constant monitoring of the amount of reactants and products, and the transfer rate (TR) of TPA into the liquid phase, are necessary for maintaining the optimal TPA/2-EH ratio, improving reaction yield, and enhancing process optimization. A safer, efficient, and faster way to monitor simultaneously multiple parameters in DOTP production is inline analysis with reagent-free near-infrared spectroscopy (NIRS). The NIRS XDS Process Analyzer by Metrohm Process Analytics enables comparison of «real-time» spectral data from the process to a reference method (*e.g.* titration, Karl Fischer titration, HPLC, ...) to create a simple, yet indispensable calibration model for your process needs.

Application: Inline analysis is possible using the properties of transflectance and the micro interactance immersion probe. The sample flows through the gap between the probe body and high-energy mirror tip, and adjusting the mirror tip defines the pathlength (equal to two times the gap) for analysis.

Remarks: An appropriate range of samples covering the process is needed to build a calibration model. These samples will be analyzed via NIR and via a reference method. The precision of the NIR data is directly correlated to the precision of the reference method. The instruments used in chemical plants are ATEX or Class 1 Div 1/2 certified. They are either mounted in the plant where they will require positive air pressure or in a pressurized shelter. The distance between the instrument or shelter and the sample points can be hundreds of meters apart. Additionally, due to the high viscosity of the reaction mixture and the shear forces present in an industrial reactor, an immersion probe with two sides is used to prevent distortion of the mirror tip.

Typical reactor composition

Components	Range (%)	Measured
2-ethylhexanol (AL)	20.4–67.9 % wt	✓
TPA pellets (AN)	0.025–31.3 % wt	✓
DOTP	0–78.4 % wt	✓
Nitrogen	0–0.006 % wt	-
Catalyst	0.072–0.078 % wt	-
Water (Moisture)	0.1–0.5 % wt	✓
AL/AN ratio	1:2	✓
Transfer rate (TR)	0–100 %	✓

NIRS XDS Process Analyzer configured for applications in ATEX areas, inset shows immersion probe.

Benefits for NIR spectroscopy in process:

- Improved product quality and manufacturing efficiency
- Reduce batch time
- Greater and faster return on investment
- Safe working environment and automated sampling

Related ASTM methods:

- **ASTM E1655**: Standard Practices for Infrared Multivariate Quantitative Analysis
- **ASTM D6122**: Standard Practice for Validation of Multivariate Process Infrared Spectrophotometers

Related Application Notes:

- **AN-PAN-1041** Inline monitoring of free isocyanate (%NCO) content in polyurethane

Related Application Bulletin:

- **AB-414** Polymer analyses using near-infrared spectroscopy

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