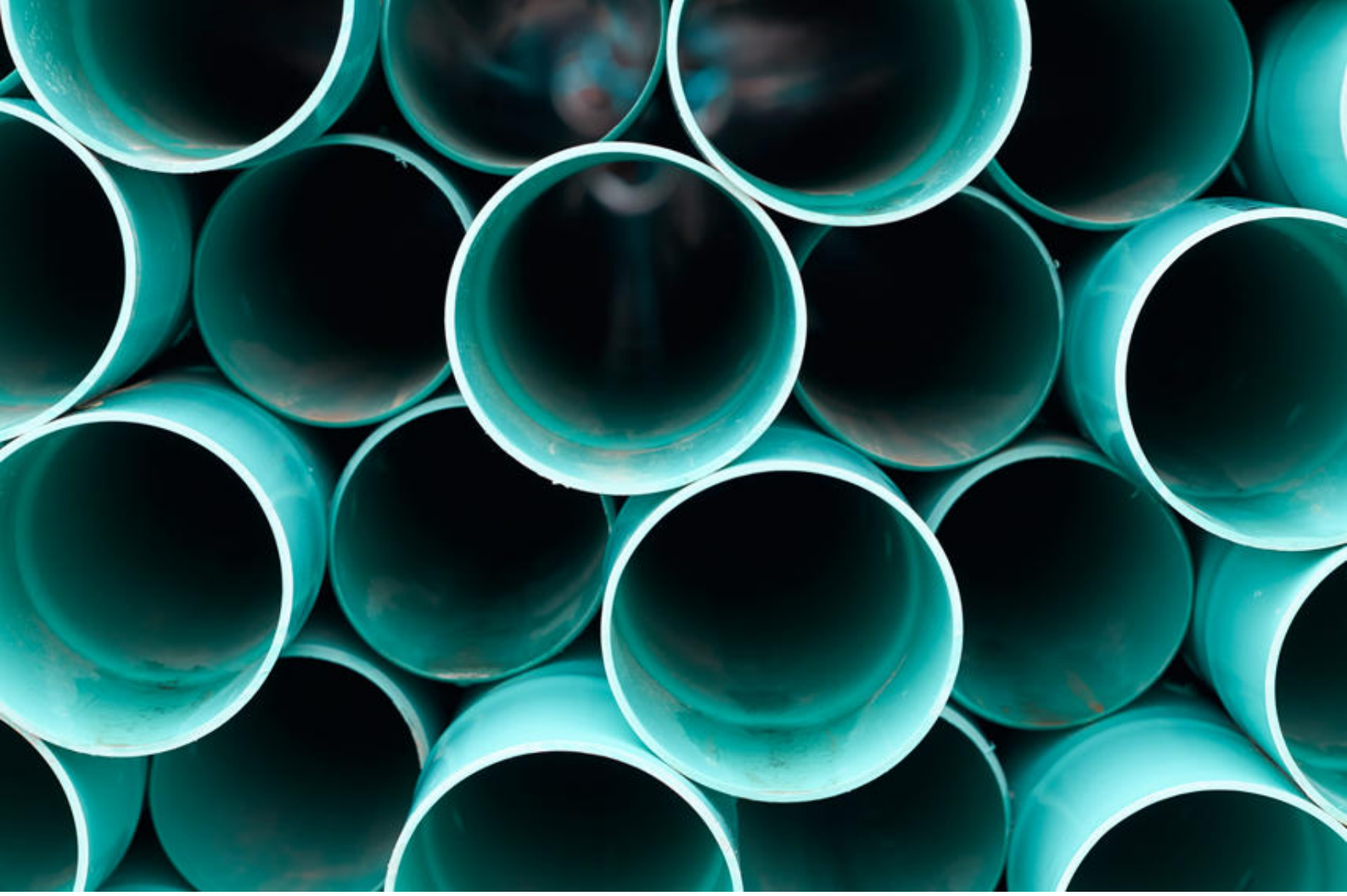


Application Note AN-PAN-1053

Monitoring of DOTP production via esterification with inline analysis

Polymers and plastics are a mainstay of modern life. Because of their versatility and physical properties, plastics and polymers are used for countless applications: in airplanes and cars, for packaging purposes, in medical devices, electronics, and much more. Without high-quality and high-tech plastics, most of the products we use today would be very different or perhaps not exist at all.

Due to growing concerns over the potential health risks associated with phthalates, there has been a global shift towards non-phthalate alternatives in the polymer industry. Dioctyl terephthalate (DOTP) is one of the most used non-phthalate plasticizers in the polymer industry since it possesses good plasticizing properties yet does not jeopardize human health.

DOTP is mainly manufactured by direct esterification. Many process parameters need to be monitored simultaneously to guarantee high product quality and high reaction throughput—something that is not possible with traditional laboratory analysis.

This Process Application Note presents a way to closely monitor multiple parameters simultaneously during the DOTP production process by using near-infrared spectroscopy (NIRS) technology.

INTRODUCTION

Polyvinyl chloride (PVC) is a polymer which is found everywhere: 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 [1]. In 2022, phthalate esters accounted for more than 3 million tons of global plasticizer consumption [2]. However, due to environmental and health risks, the world use of non-phthalate ester plasticizers is expected to increase to around 2.6 million tons [2].

The non-phthalate plasticizer dioctyl terephthalate (DOTP or DEHT), is an organic molecule with the chemical formula $C_6H_4(CO_2C_8H_{17})_2$. This colorless viscous liquid is known to be a great substitute for harmful phthalates in plastic production.

One of the methods of manufacturing DOTP is by direct esterification of purified terephthalic acid (TPA) and the branched-chain 2-ethylhexanol (2-EH) [3]. TPA comes in pelleted form, 2-EH as a liquid solution, and they are mixed together in an industrial reactor in a 1:2 ratio. A catalyst is added, and the temperature is maintained between 160 °C and 235 °C for a few hours. During this time, DOTP is formed along with water, which is removed to keep the moisture content low over the course of the reaction. High-purity DOTP is obtained through this process.

Many parameters need to be monitored in order to guarantee a high reaction yield and high DOTP quality. Traditionally, the amount of reactants and products are measured in the laboratory after taking a sample from the production process.

However, manual laboratory methods can give long response times which are not ideal in the case of process changes (e.g., reaction mixture, moisture levels). Moreover, sample preparation (e.g., dilution, filtration, pipetting) can introduce errors that alter the precision of the analysis. Manual laboratory work can be quite cumbersome in this case 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 (Figure 1).

An improved, more effective, and quicker method for simultaneously monitoring various parameters throughout the production of DOTP involves utilizing

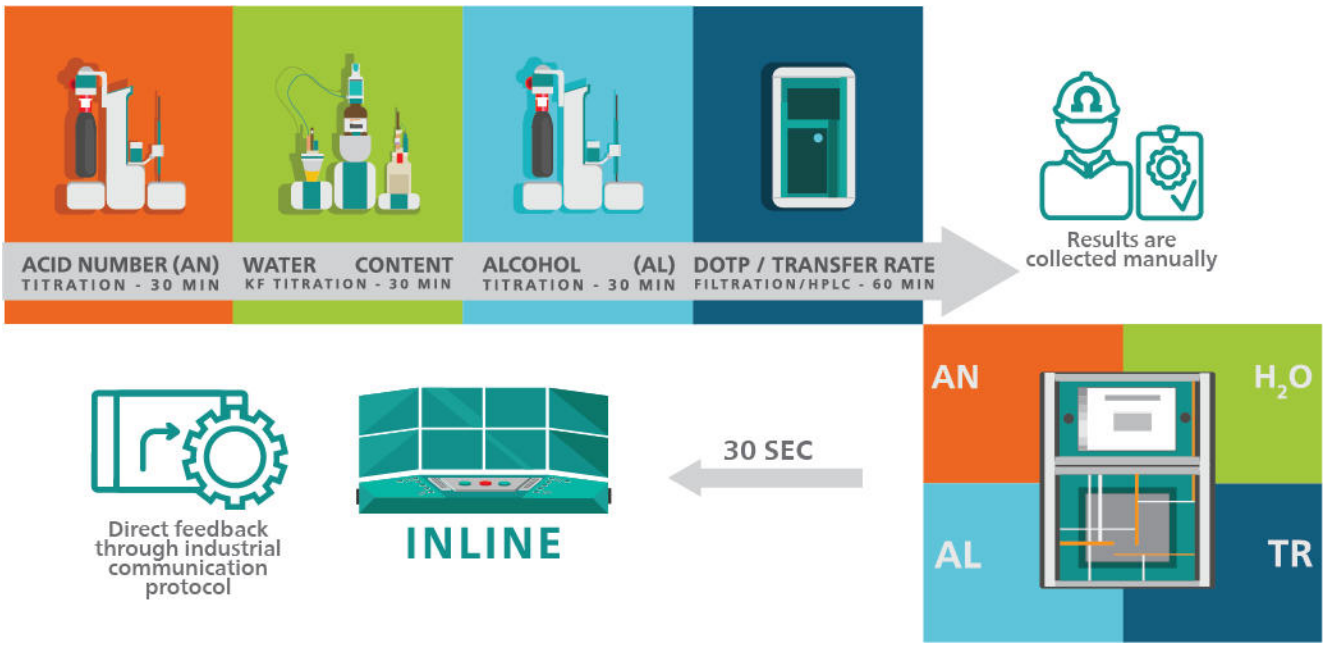


Figure 1. Steps to measure important parameters in DOTP production by implementing offline (top) or inline (bottom) analysis procedures.

APPLICATION

Inline analysis of multiple quality parameters is possible with NIRS 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 (Figure 2). An adjustment of this mirror tip defines the pathlength which is equal to two times the gap for precise analysis.

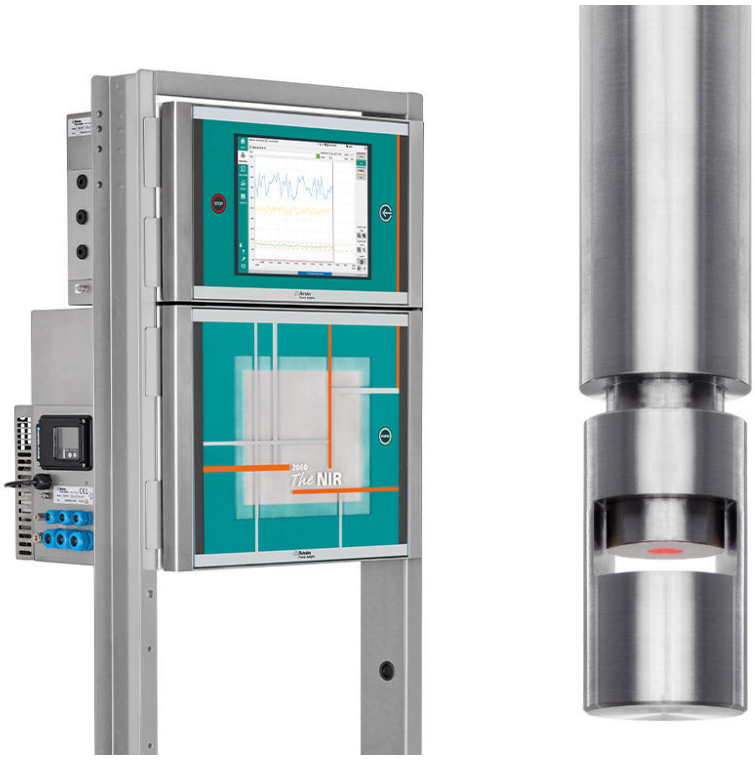


Figure 2. 2060 The NIR-Ex Analyzer configured for applications in ATEX areas; inset shows the immersion probe.

Table 1. Typical DOTP reactor composition.

Component	Range	Measured by NIRS
2-ethylhexanol (AL)	20.4–67.9 % wt	✓
TPA pellets (AN)	0.025–31.3 % wt	✓
DOTP	0–78.4 % wt	✓
Water (Moisture)	0.1–0.5 % wt	✓
AL/AN ratio	1:2	✓
Transfer rate (TR)	0–100%	✓

TYPICAL RANGES

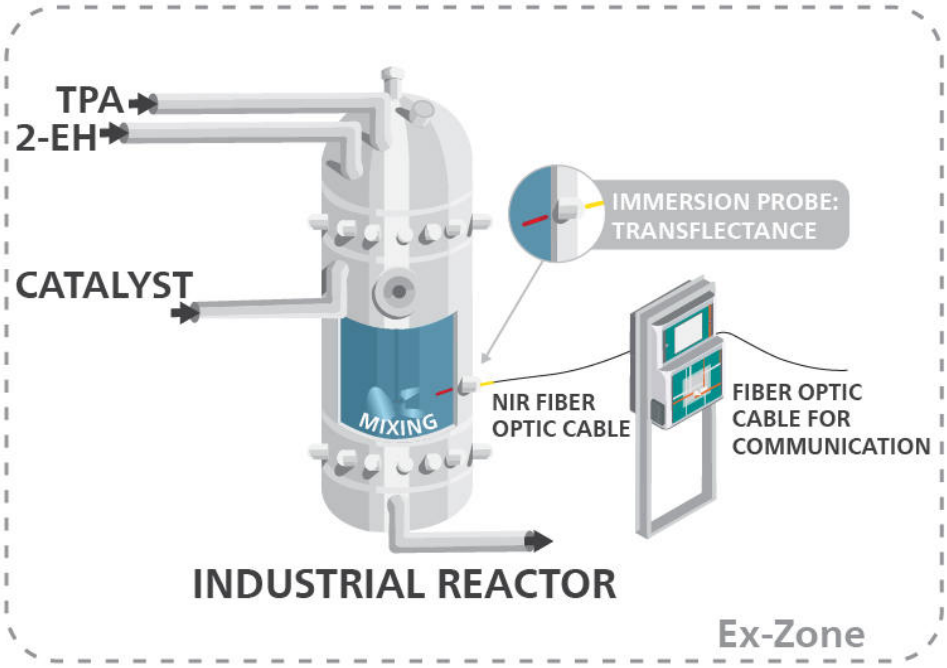


Figure 3. Illustration of suggested placement for near-infrared (NIR) probe in an industrial DOTP reactor.

REMARKS

To construct a calibration model, a suitable variety of samples that represent the process is required. These samples will be examined using NIRS and a benchmark method. The accuracy of the NIRS data is directly linked to the accuracy of the benchmark method.

The devices used in chemical factories are certified by ATEX or Class 1 Div 1/2. They are either installed in the factory where they require positive air pressure or are housed in a pressurized shelter. The distance between the device or shelter and the sample locations can span hundreds of meters. Furthermore, due to the high viscosity of the reaction mixture and the shear forces in an industrial reactor, a two-sided immersion probe is utilized to avoid distortion of the mirror tip.

CONCLUSION

Keeping a close watch on the quantity of reactants and products, as well as the transfer rate (TR) of TPA into the liquid phase, is crucial for maintaining the ideal TPA/2-EH ratio (AL/AN ratio, Table 1). This boosts the DOTP reaction yield and helps to optimize the production process.

A more secure, effective, and quicker method to concurrently monitor multiple parameters in DOTP production is with inline process analysis using reagent-free near-infrared spectroscopy (NIRS). The 2060 *The* NIR-Ex Analyzer by Metrohm Process Analytics (Figure 2) allows «real-time» spectral data from the process to be compared with a reference method (e.g., titration, Karl Fischer titration, HPLC) to establish a straightforward, yet essential calibration model for process monitoring and improvement.

BENEFITS FOR NIR SPECTROSCOPY IN PROCESS

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



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3. Harmon, P.; Otter, R. A Review of Common Non-Ortho-Phthalate Plasticizers for Use in Food Contact Materials. *Food and Chemical Toxicology* **2022**, *164*, 112984. https://doi.org/10.1016/j.fct.2022.112984.

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 NOTE

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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CONFIGURATION



2060 The NIR-Ex Analyzer

Le 2060 *The* NIR-Ex Analyzer est la nouvelle génération d'appareils de spectroscopie de processus de Metrohm Process Analytics. Avec sa conception unique et éprouvée de l'intérieur vers l'extérieur, il fournit des résultats précis toutes les *10 secondes*. Il peut fournir une analyse non destructive des liquides et des solides directement dans la ligne de traitement ou dans une cuve à réaction en utilisant des fibres optiques et des sondes de contact. Il a été concu pour connecter jusqu'à cinq (5) sondes et/ou cellules à circulation. Chacun des cinq canaux peut être configuré indépendamment des autres à l'aide de notre logiciel propriétaire embarqué polyvalent.

De plus, cet appareil d'analyse est certifié IECEx et est conforme aux directives européennes ATEX. Il a été concu avec un système de purge/pressurisation approuvé ainsi que des dispositifs intrinsèquement électroniques, empêchant toute fumée ou gaz potentiellement explosifs de l'air ambiant de pénétrer dans l'enceinte de l'appareil d'analyse. De plus, il est disponible en trois autres versions : le 2060 *The* NIR Analyzer, 2060 *The* NIR-R Analyzer et 2060 *The* NIR-REx Analyzer.