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

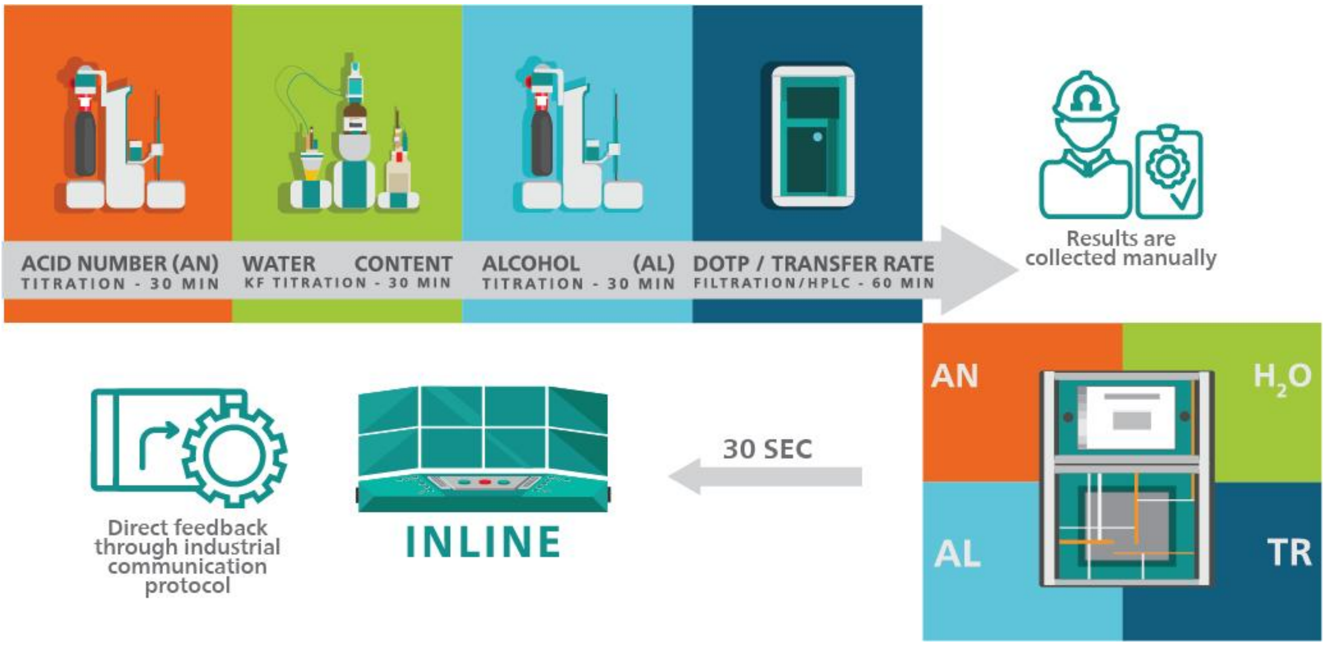

Figure 1. Steps to measure important parameters in DOTP production by implementing offline (top) or inline (bottom) analysis procedures.

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.

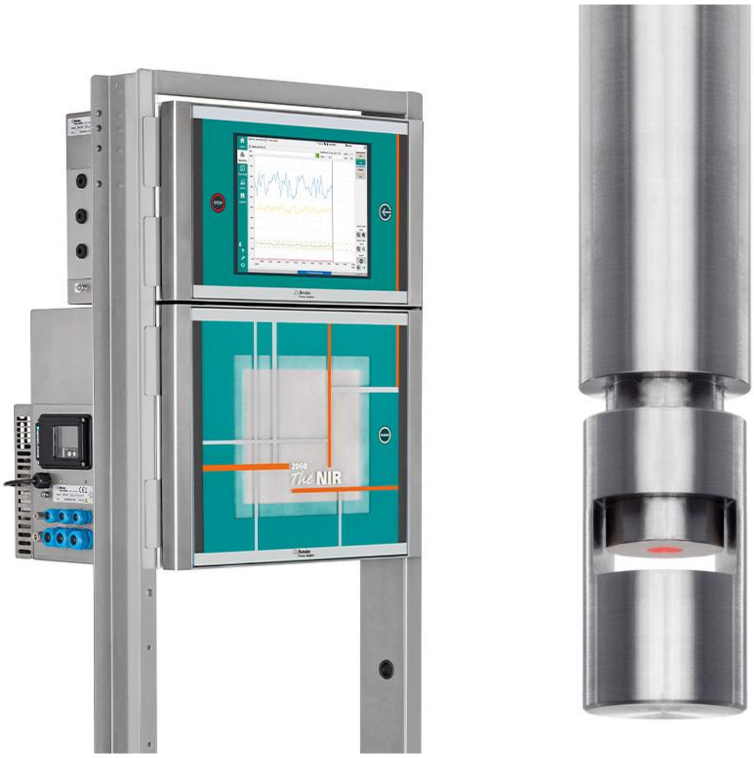

Figure 2. 2060 The NIR-Ex Analyzer configured for applications in ATEX areas; inset shows the immersion probe.

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%	✓

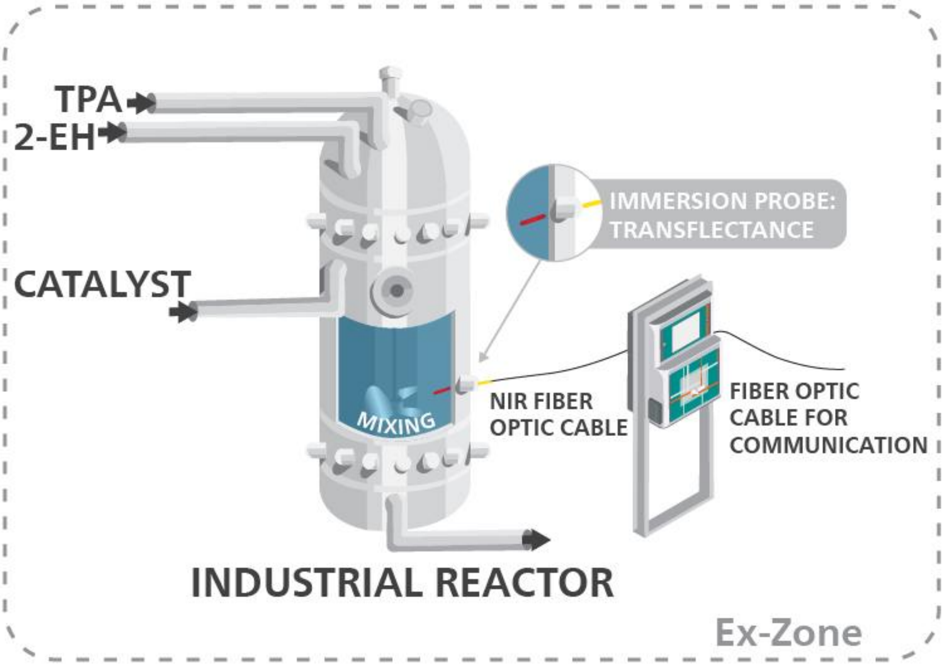

Figure 3. Illustration of suggested placement for near-infrared (NIR) probe in an industrial DOTP reactor.

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

REFERENCES

1. *Plasticizers. CHEMICAL ECONOMICS HANDBOOK*. S&P Global. https://www.spglobal.com/commodityinsights/en/ci/products/plasticizers-chemical-economics-handbook.html (accessed 2023-09-28).
2. Market Report Plasticizers: Industry Analysis | 2022-2032. *Ceresana Market Research*.
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

2060 *The* NIR-Ex Analyzer は、Metrohm Process Analytics 製の次世代フロセス分光法措置てす。その独自て定評のある完全な設計により、*10 秒*ことに正確な結果を出します。この装置は、光ファイハーまたは接触式フローフを用いた、フロセスラインまたは反応容器における直接液体または固形物の非破壊分析を提供します。五 (5) つまてのフローフおよひ/またはフローセルを接続てきるように設計されています。弊社独自開発の多機能な組込ソフトウェアを使用して、5 つのチャンネルをすへて互いに独立して設定することかてきます。

加えて、このアナライサーは IECEx 認証を取得し、ATEX EU 指令を満たしています。本装置は、あらゆる潜在的な爆発性ヒュームまたはカスか周囲の空気からアナライサーのカハーに入り込むのを防く、本質的な電子装置とともに、検定済みハーシ/加圧システムて設計されています。さらに、他の三つのハーションて使用可能てす: 2060 *The* NIR Analyzer、2060 *The* NIR-R Analyzer、 およひ 2060 *The* NIR-REx Analyzer。