Monitoring of DOTP production via esterification with inline analysis

Summary

Polymers and plastics are a mainstay of modern life. Because of their versatility and physical properties, plastics and polymers have conquered nearly every aspect of human activity: airplanes and cars, packaging of all kinds, medical devices and products, electronics, and countless more. Without high-quality and high-tech plastics, most of the products we use today would look very different.

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, and many 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 via near-infrared spectroscopy (NIRS) technology.

Introduction

Polyvinyl chloride (PVC) is a plastic polymer which is seen 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 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.

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 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 ^{o}C and 235 ^{o}C for a few hours. During this time, DOTP is formed together 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 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 (e.g., 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 (**Figure 1**).

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

Configuration

A629280130C - NIRS XDS Process Analyzer – MicroBundle 9 Channels

The NIRS XDS Process Analyzer – MicroBundle provides the next generation of process analyzers for real-time analysis in the pharmaceutical and chemical industries. Non-destructive, accurate measurements of practically any sample type (powders, slurries, liquids,..) are performed directly in the process line, granulator, dryer or reaction vessel. Up to 9 probes and/or flow-cells can be connected to the analyzer. All 9 channels can be configured independently from each other and the micro bundle fiber optics allows the 9 measuring points to be up to 35 meter away from the XDS NIR process analyzer.

Application

Figure 2. NIRS XDS Process Analyzer configured for applications in ATEX areas, inset shows immersion probe.

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. An adjustment of this mirror tip defines the pathlength which is equal to two times the gap for precise analysis.

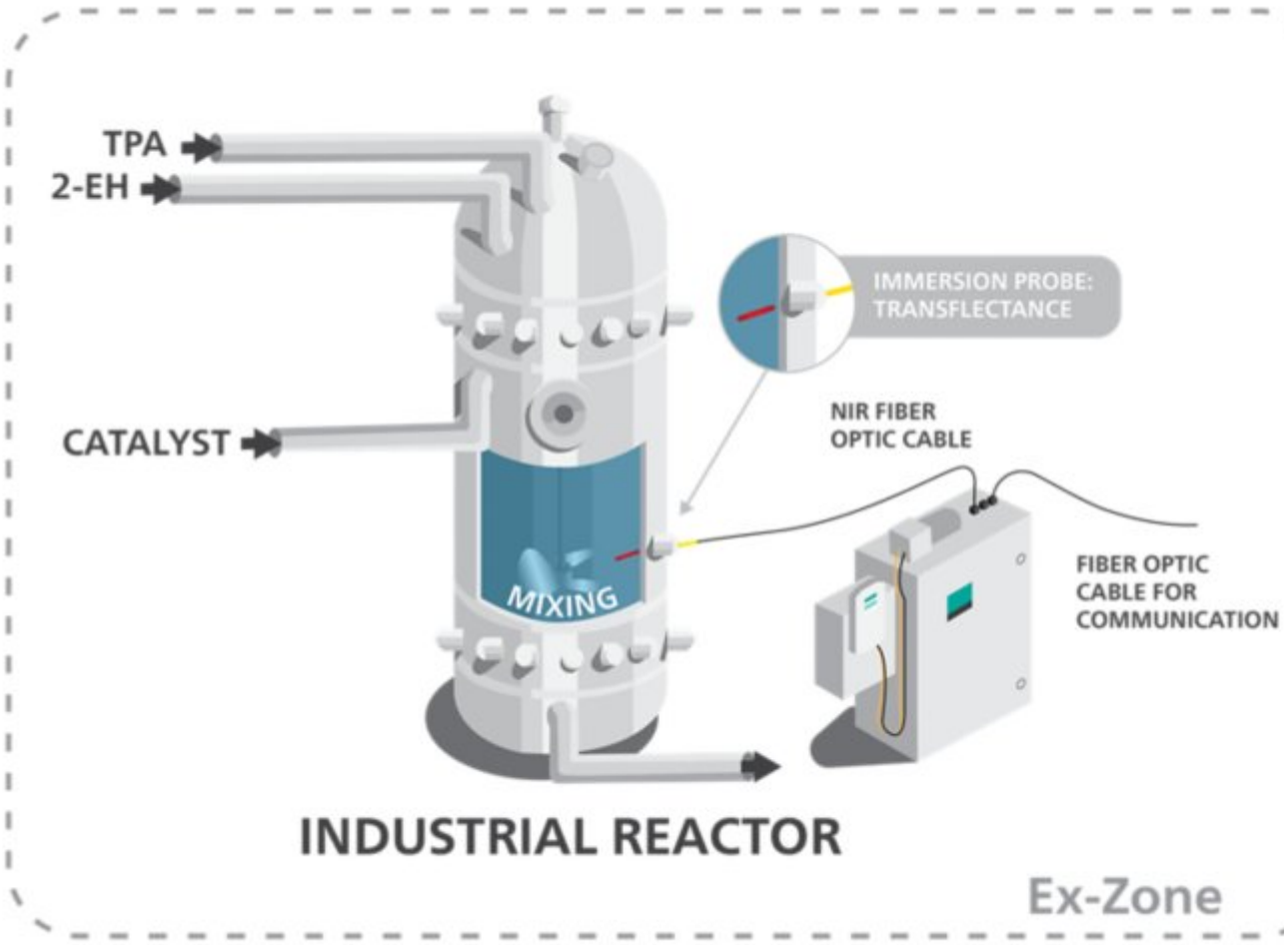

Figure 3. Stylization of suggested placement for near-infrared (NIR) probe in an industrial DOTP reactor.

Table 1. 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	
Water (Moisture)	0.1–0.5 % wt	
AL/AN ratio	1:2	
Transfer rate (TR)	0–100%	

Conclusion

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 simultaneously monitor multiple parameters in DOTP production is inline analysis with reagent-free near-infrared spectroscopy (NIRS). The NIRS XDS Process Analyzer by Metrohm Process Analytics (**Figure 2**) 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.

Remarks

An appropriate range of samples covering the process is needed to build a calibration model. These samples will be analyzed via NIRS and via a reference method. The precision of the NIRS 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.

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

Further reading

Related application documents

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

AB-414 Polymer analyses using near-infrared spectroscopy

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