

Online monitoring of TBC in styrene storage tanks according to ASTM D4590

In the production of styrene, butadiene, and vinyl acetate, the stabilizer 4-*tert*-butylcatechol (TBC) plays a crucial role in preventing premature polymerization during storage and transport.

In order to guarantee product quality, the TBC concentration in styrene must be maintained

above 10–15 mg/L. Close monitoring of the concentration is necessary to control TBC levels.

This Process Application Note presents a solution for online colorimetric determination of TBC in styrene (as per ASTM D4590) with the **2060 TI Ex Proof Process Analyzer** from Metrohm Process Analytics.

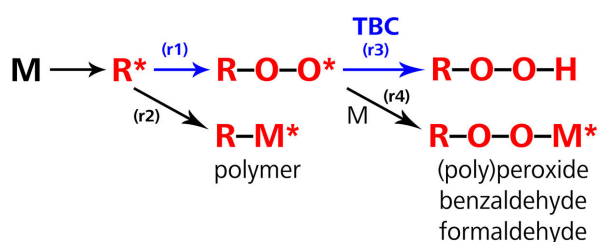
INTRODUCTION

More than 27 million tons of styrene monomer ($C_6H_5CH=CH_2$) are produced worldwide each year [1]. Styrene and other reactive monomers, such as butadiene and vinyl acetate, are inherently unstable during storage and transport due to their tendency to undergo spontaneous polymerization when exposed to environmental

triggers like heat, light, or oxygen.

Chemical stabilizers like 4-*tert*-butylcatechol are added to mitigate this risk. TBC acts as a free radical inhibitor to prevent the formation of long polymer chains that can lead to viscosity changes, blockages, or even runaway reactions in storage tanks.

(r1) and (r3) are fastest if $[O_2]$ and [TBC] are sufficient



Reaction 1 Mechanism for the inhibition of polymer formation in styrene monomer with the addition of TBC and oxygen.

These contaminations can be hazardous during the purification processes (distillation) due to the instability of peroxides at increased temperatures. Therefore, the TBC concentration in styrene must be maintained above 10–15 mg/L. Close monitoring of the TBC concentration is required to control its

Styrene monomers (M) form radicals (R^*) when they are exposed to either light or heat (**Reaction 1**). These radicals can react with either oxygen (causing peroxide radicals) or other monomers to create polymer chains. This polymerization is exothermic. If left uncontained, it can lead to runaway polymerization in the styrene storage tank, resulting in serious consequences.

TBC is a free radical inhibitor that requires oxygen to prevent the monomers from polymerizing. Because monomers are present in the solution and in the tank headspace, a minimum concentration (10–15 mg/L) of oxygen (O_2) is required in both.

The O_2 addition is necessary to take advantage of different reaction kinetics (**Reaction 1**) – peroxide radical formation (r1) occurs much faster than styrene polymer formation (r2). In the presence of the correct amount of TBC, these peroxide radicals are scavenged (r3). Otherwise, the peroxide radicals react with styrene monomers to form peroxide chains (polyperoxides, r4) until the oxygen is completely depleted.

depletion.

While TBC is essential for preventing styrene and other reactive monomers from polymerizing prematurely, solely relying on laboratory analyses might be inadequate to guarantee consistent TBC levels within the required range. Furthermore, the delay between sample

collection, analysis, and results further magnifies the challenge of promptly addressing any deviations from optimal TBC concentrations. For operators tasked with maintaining TBC levels above the critical threshold of 10–15 mg/L, a more responsive and continuous monitoring approach is important to mitigate the risk of polymerization incidents and maintain product quality throughout the entire storage and

APPLICATION

The method used is based on ASTM D4590 for the colorimetric analysis of 4-*tert*-butylcatechol

transportation process. A photometric process analyzer accurately tracks TBC reduction at the styrene storage tank inlet to maintain optimal conditions around the clock. Metrohm Process Analytics offers the **2060 TI Ex Proof Process Analyzer** for monitoring TBC concentration in styrene (Figure 2).

(TBC) in styrene. The results are calculated based on a photometric determination at 490 nm.

Table 1. Parameter to monitor in styrene storage.

Parameter	Concentration [mg/L]
4- <i>tert</i> -butylcatechol (TBC)	0–50

REMARKS



Due to styrene’s sensitivity to light and heat, storage conditions can quickly become hazardous. Continuous monitoring is essential. In hazardous environments, only explosion-proof analyzers like the **2060 TI Ex Proof Process Analyzer** (Figure 2) ensure safe, real-time TBC control.

Figure 2. 2060 TI Ex Proof Process Analyzer for monitoring TBC in styrene.

CONCLUSION

Online monitoring of TBC, as defined in accordance with ASTM D4590, is essential for maintaining product quality and safety during the production and storage of styrene, butadiene, and vinyl acetate. The presence of TBC prevents early polymerization, thereby avoiding potential hazards associated with unwanted polymerization reactions. Maintaining TBC concentrations above the

critical threshold of 10–15 mg/L is crucial. This requires close and continuous monitoring. Online process analyzers, such as the **2060 TI Ex Proof Process Analyzer** from Metrohm Process Analytics (configured for photometric analysis), offer a reliable solution for real-time TBC concentration monitoring. This ensures optimal storage conditions and product quality.

RELATED APPLICATION NOTES

[AN-PAN-1007](#) Online analysis of peroxide in the HP-PO process

[AN-PAN-1041](#) Inline monitoring of free

[isocyanate \(%NCO\) content in polyurethane](#)

[AN-PAN-1053](#) Monitoring of DOTP production via esterification with inline analysis

OTHER RELATED DOCUMENTS

[WP-048](#) Utilizing online chemical analysis to

[optimize propylene oxide production](#)

BENEFITS FOR ONLINE PROCESS ANALYSIS

- **Optimize product quality** and increase profit with fast response times to variation in process conditions.
- **Fully automated diagnostics**—automatic alarms for when TBC concentrations are outside of the specified parameters.
- **Safe working environment** and automated sampling.



REFERENCE

1. Falcke, H.; Holbrook, S.; Clenahan, I.; et al.
Best Available Techniques (BAT) Reference Document for the Production of Large Volume Organic Chemicals. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). JRC Publications Repository.
<https://publications.jrc.ec.europa.eu/repository/handle/JRC109279> (accessed 2024-03-06).
<https://doi.org/10.2760/77304>

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CONFIGURATION



2060 TI Ex Proof Process Analyzer

2060 TI Ex Proof Process Analyzer は、ガスまたは粉塵の危険区域（ゾーン 0、1、2、または 20、21、22）におけるプロセスモニタリング用の本質安全防爆型湿式化学プロセスアナライザーです。EU指令 94/9/EC (ATEX95) に準拠し、ゾーン 1 およびゾーン 2 区域での使用が認証されています。その設計では、パージ・加圧システムと本質安全防爆電子機器が組み合わされています。エアパージの段階と恒常的な過圧で、爆発性雰囲気のアナライザーのカバーへの侵入を防止します。

本アナライザーの設計により、大型アナライザーシールドのパージが不要となり、危険区域内の製品ラインへの直接の取り付けが可能となります。滴定やカール・フィッシャー滴定、測光、イオン選択性電極測定、直接測定を含む各種の技術に対応しています。