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Mitigating butadiene popcorn formation in industrial olefin units

Aim

Mitigating butadiene popcorn formation in industrial olefin units.

Justification

Olefin units are subject to fouling and corrosion. Intrusion of molecular oxygen in distillation towers and overhead condensers forms peroxides, which initiate (and catalyze) butadiene polymerization. The mechanism is initiated by air or peroxides and promoted by rusty iron, oxygen and metal oxide catalysts. Butadiene polymer may appear in different forms, namely sheet, rubber, crystalline, or popcorn polymer. The latter is insoluble and hence detrimental to many unit operations. In addition, popcorn polymer presents a safety issue, as it rapidly and powerfully expands, building up pressure, resulting in popcorn particles "popping" and causing mechanical damage such as metal rupture, leading to loss of containment. Hence, olefin units typically have spare depropanizer reboilers to ensure a *ca.* 4 year on-line cycle, with a cycle time of *ca.* 12 months for the reboiler. Fouling occurs mostly in the reboiler and less in the depropanizer bottom. Since the 1940s, butadiene unit operators have learnt that certain process conditions exacerbate popcorn formation, yet no comprehensive model exists to predict reported popcorn reactivity behavior.

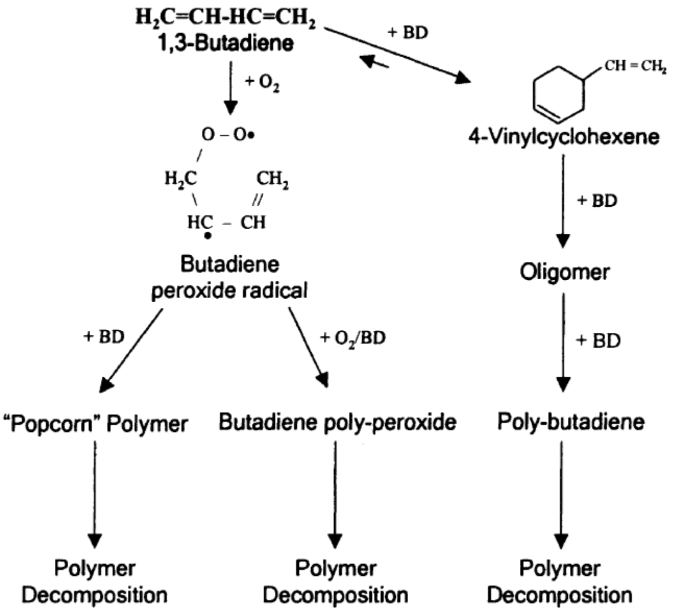

Figure 1: Reaction mechanism for 1,3-butadiene. Adopted from Levin et al. *Journal of Hazardous Materials* **2004**, 115, 71–90.

Program

1. Literature study to identify the industrial shutdown protocols which cause popcorn formation.
2. Improve the existing design of glass vials in order to mimick the conditions of *e.g.* industrial reboilers (in cooperation with EEPC members, in particular Dow Terneuzen).
3. Synthesize popcorn in glass vials to identify which industrial shutdown/cleaning protocols cause popcorn formation.
4. Determine the role of oxygen in the initiation mechanism responsible for popcorn formation.
5. Characterization of the morphology of the synthesized popcorn using Raman spectroscopy.

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