

Oxidation of Copper-Based Adsorbents

The following guideline applies to PuriStar R3-15 and R3-16 used typically in Ethylene Service

Introduction

PuriStar® R3-15 and R3-16 are used for the conversion of CO and H₂, which can be present in trace amounts in ethylene. For application details, please refer to the respective datasheets.

During the use in this service the adsorbents will become reduced. To allow for proper regeneration of the adsorbents a re-oxidation step is required. Details of this treatment are described in the following.

Another use of these materials is the removal of oxygen. Here the adsorbent needs first to be reduced to allow for uptake of oxygen. To ensure that the material is in its fully oxidic state before unloading, it is recommended to do a complete re-oxidation of the material.

The re-oxidation can be described by the following reaction:



The re-oxidation is typically carried out by passing a non-reactive (inert) gas (e.g. nitrogen) into which is mixed air through the bed at temperatures of 180°C (360°F), preferably at a space velocity of 300 hr⁻¹ (GHSV). To avoid any fluidization of the bed,

the re-oxidation is typically carried out in down-flow. Temperatures in the bed should be limited to 230°C (450°F), to avoid any irreversible deterioration of the adsorbent.

Before initial operation of these adsorbents, only a drying procedure is required.

Please refer to the respective guideline for more information.

Monitoring of the progress of the oxidation can be done by closely following the temperatures at the inlet, outlet and in the bed and by determining the consumption of O₂ (measuring the inlet and outlet concentration).

During the oxidation of the partially or completely reduced Cu, certain amounts of CO, CO₂ and H₂O and some higher hydrocarbons can also be released. This is due to the conversion and combustion at higher temperatures of polymeric hydrocarbon deposits on the bed, which can accumulate over time.

Safety

To control the temperature during the oxidation, air is mixed with inert gases, like nitrogen. The flow rates of both gases must be tightly controlled to avoid any temperature excursion. To cap the maximum flow of air,

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installing orifice plates, limiting the feed pressure or other measures can be considered. Alternatively, also the O₂ concentration in the inert gas can be monitored and limited.

It is preferable to have some more temperature measurements along the bed length. When installing these measurements, it must be assured that the measurements are really located in the bed to be reduced.

The respective temperature measurements should be used to protect the mechanical integrity of the vessel by using them also for switches which become active when excessively high temperatures are measured. Protective switches linked to these temperature measurements should shut down any heat source used for heating the gas flow fed to the vessel as well as stopping the air flow. The flow of inert gas must be maintained to assure proper cooling of the bed.

When choosing an inert carrier gas, the inert gas or components thereof must have no reaction with oxygen, (reduced) copper or copper oxide.

Typical examples of stream component reactions occurring with O₂ in the presence of copper are:

(1) O₂ + Hydrocarbons → CO/CO₂/H₂O (exothermic)

(2) O₂ + Hydrocarbons → Partially decomposed hydrocarbons (exothermic)

(3) O₂ + H₂ → Water (exothermic)

(4) O₂ + CO → CO₂ (exothermic)

(5) O₂ + C → CO/CO₂ (exothermic)

Oxidation (Regeneration) Procedure

This procedure is designed to oxidize a 10 m³ bed of PuriStar R3-15 or R3-16 in approx. 2-3 days. Higher or lower space velocities will result in shorter or longer oxidation times. However, the gas flow (Air + N₂) should be no less than 3,000 Nm³/hr (GHSV=300 hr⁻¹) to insure good gas distribution and reaction efficiency.

1. Establish a flow of Nitrogen at 3750 kg/hr = 3000 Nm³/hr. Maintain this flow throughout the entire procedure. No preheating is required before proceeding to Step 2 and initiating the injection of Air.

2. Begin Air rate at approx. 50 kg/hr to provide an initial inlet O₂ concentration of around 0.25 mol%.

3. Begin ramping up the inlet temperature slowly, by 25-35°C per hour, until the inlet temperature reaches 160°C (320°F). Hold this inlet temperature and Air rate of approx. 50 kg/hr for an additional 5 hours.

4. Increase the Air rate to around 100 kg/hr to provide an inlet O₂ concentration of around 0.5 mol%. Hold this Air rate for at least 24 hours or until all temperature points in the bed are stable and indicating no exotherm from oxidation reactions of the catalyst or of any hydrocarbons.

5. Increase the Air rate to 150 kg/hr. Now, the O₂ level in the feed is approx. 0.75 mol%. Hold this Air rate for at least 24 hours or until all temperature points in the bed are

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stable and indicating no exotherm from oxidation reactions of the catalyst or of any hydrocarbons.

6. Increase the Air rate to 200 kg/hr. This will bring the inlet O₂ level up to around 1 mol%, which is the highest concentration indicated in this procedure. Hold these conditions for at least 24 hours.

7. Decrease the Air rate to 100 kg/hr and then bring up the temperature to 180°C (360°F). This will get the inlet O₂ level to around 0.5%. Hold these conditions for at least 10 hours.

8. After stoppage of air flow, maintain bed temperature of 180°C (360°F) for 4 hours with N₂ flow before starting the cool-down, to remove the bulk of any adsorbed moisture which may have been formed by combustion of hydrocarbon deposits, before starting the cool-down.

9. Now, decrease the inlet temperature of the nitrogen down by maximum 50°C per hour until the inlet gas temperature is down to around ambient temperature (although the operating temperature is closer to 100°C (210°F), it's prudent to cool to a lower temperature to be sure there are no hotspots before putting the bed back in service.) The bed is now ready to be put back into service, after filling the bed with ethylene and achieving operation temperature of 85-90°C (185-195°F).

Additional Notes

a) As mentioned in the preface notes, there may be exotherms from oxidation of hydrocarbon deposits on the catalyst, particularly once the bed temperatures are >150°C (300°F). In case O₂ levels have been

increased to > 1% (whether by accident or by issues in flow measurement or control), this could lead to excessively high temperatures which could damage the catalyst. Bed temperatures should be monitored closely throughout the procedure. In case of excessively high or sharply rising temperatures, as a first step shut off the air for a short time (one hour should be long enough), to allow cooling of the hotspot by the N₂ flow. Preferably do not exceed 230°C (450°F) (in the bed at any time.

b) The oxidation of Cu does not produce any water. However, if there is oxidation of hydrocarbons some water can be produced from this combustion. The 4-hour hold at 180°C (355°F) after stoppage of air injection will ensure that the bed is dry before cooling down.

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Americas

BASF Corporation
25 Middlesex/Essex Turnpike
Iselin, New Jersey, 08830, USA
Tel : +1-732-205-5000
Fax: +1-732-205-7725
Email: catalysts-america@basf.com

Asia Pacific

BASF (China) Company Limited
300 Jiang Xin Sha Road,
Pudong, Shanghai 200137
P.R. China
Tel: +86-21-2039 2549
Fax: +86-21-2039 4800-2549
Email: catalysts-asia@basf.com

Europe, Middle East, Africa

BASF De Meern BV Catalysts
The Netherlands
Tel: +31-30-666 9437
Email: catalysts-europe@basf.com

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