

Loading, Start-up and Regeneration Procedures for BASF PuriStar® R 3-17RED

I. Introduction and Operating Principle

BASF Catalyst PuriStar® R 3-17RED represents a newly developed technology for the removal of trace levels of **Carbon Monoxide** (CO), which are typically around 500 ppb-vol. or less, from **Liquid Hydrocarbons**; and in particular, from polymer grade propylene.

The heart of the technology is a special tablet-form catalyst containing CuO, ZnO and ZrO₂ plus promoters. CO removal is achieved by flowing the liquid hydrocarbon through a fixed bed of the catalyst at mild temperatures, typically 20-40°C.

The R3-17RED is delivered pre-activated and is ready for use. Once delivered to the customer, the catalyst can be operated with no further pre-treatment.

As CO comes in contact with the surface of the catalyst, CO removal is effected by reaction of CO with surface sites of the activated metal oxide matrix; the CO thus removed is in a further oxidized state and remains on the surface of the catalyst until regeneration. During regeneration the removed CO is rejected from the catalyst bed in the form of CO₂ which is carried out by the regeneration gas.

Due to capacity factors and on-stream requirements, two vessels are generally required for continuous operation; one vessel is in operation, the other in standby or being regenerated.

II. Loading of the Catalyst

Although the primary purpose of the partial oxidation (step 2 of the factory activation procedure) is to achieve optimum activity for CO removal, it also provides some passivation, such that a brief (less than 1 h) exposure to stagnant air at ambient temperature should not cause significant heating of the catalyst. Nevertheless, IT IS ESSENTIAL TO AVOID OXIDATION OF THE CATALYST DURING LOADING, otherwise its performance may be adversely affected. Therefore, minimizing contact of the catalyst with air, and excluding air from the reactor vessel once catalyst loading has commenced, is a critical requirement for a successful loading.

Loading of the catalyst into the vessels, should be consistent with the following guidelines:

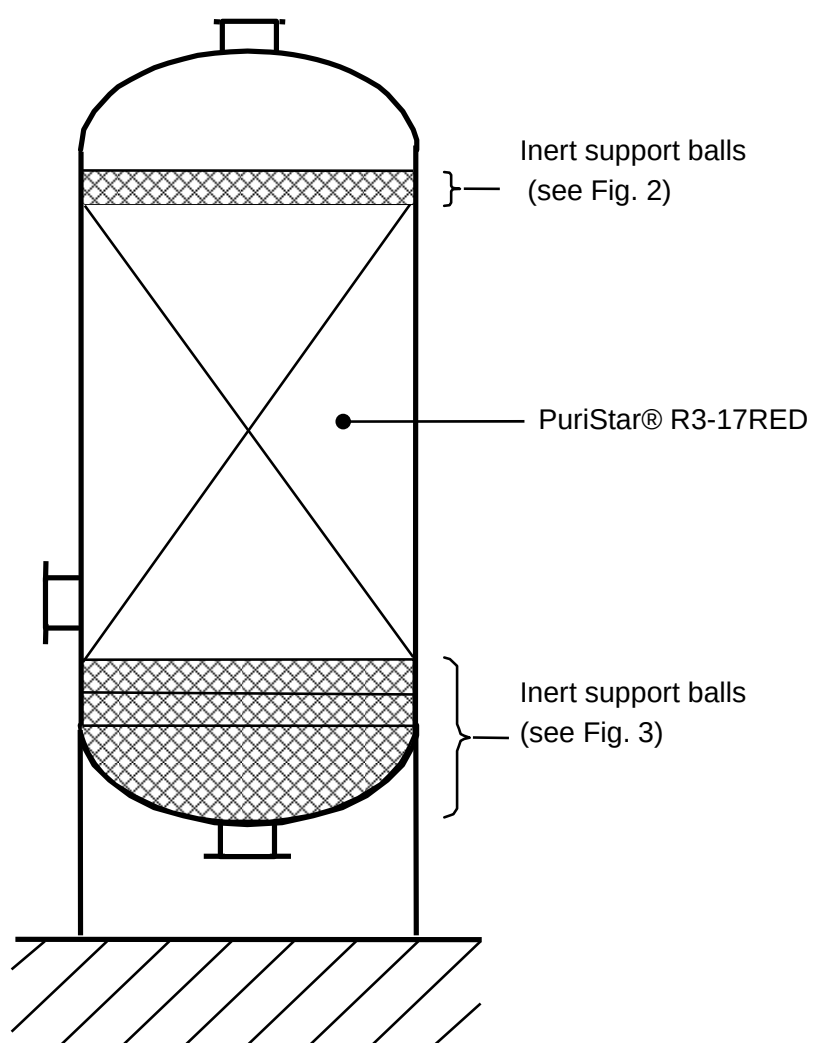


The Chemical Company

1. Before the catalyst is charged, the vessel should be cleaned, leak-tested, and inspected. The inside walls and any internals must be clean. The condition of the vessel (if not new) should be noted with respect to corrosion and wall thickness.
2. Before charging catalyst to the vessel, it is recommended to mark the inside wall of the vessel with chalk or soap at the targeted heights for the layers of support material, catalyst and hold-down balls respectively. This will facilitate leveling of the bed, and will also assist in getting the correct quantities of materials loaded.
3. A suitable bed support must be installed before catalyst loading begins. See Figures 1 - 3 for a typical bed support design. Any dumped support must be leveled before adding the catalyst.
4. Either before or after installing the bed support, but before beginning to charge the catalyst itself, the atmosphere inside the vessel must be made inert, by purging with nitrogen and/or pressurizing/depressurizing repeatedly with nitrogen, until the oxygen content is below 100 ppm. From this point on, a moderate nitrogen sweep from bottom to top should be maintained throughout the catalyst loading, and any personnel working inside the vessel or on the platform above the vessel must use a breathing air mask in order to avoid the hazard of asphyxiation.
5. The catalyst can be charged directly from drums, or from a loading hopper. If loading hoppers are used they must be nitrogen-purged before catalyst is placed inside, and kept air-free to avoid oxidation of the catalyst. Only 1 drum at a time should be opened, and it should be emptied immediately and with minimal air contact, into the hopper or reactor.
6. The catalyst must not be allowed to free-fall more than 1 meter. The free-fall can be controlled by loading through a funnel with attached hose (hence "sock-loading"). Pinching down on the end of the hose to keep the hose full of catalyst is advised.
7. If personnel must be inside the vessel during the filling or at any time after catalyst loading has commenced, boards should be placed on top of the catalyst for the workers to stand on. Treading directly on the catalyst should be avoided, as this can lead to attrition and the creation of catalyst fines in the bed.
8. After all catalyst has been loaded into the reactor vessel, the bed must be leveled.

9. Finally, the hold-down layer of inert balls (see Figure 2) must be put in and leveled, then the vessel closed and purged further with nitrogen to remove any oxygen which may be present in the vessel's atmosphere.

Figure 1



Bed support and hold-down illustration (continued)

Figure 2. Bed hold-down detail

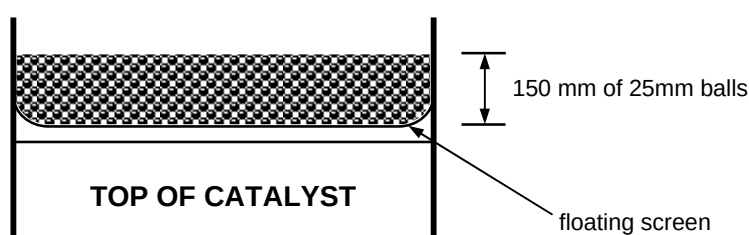
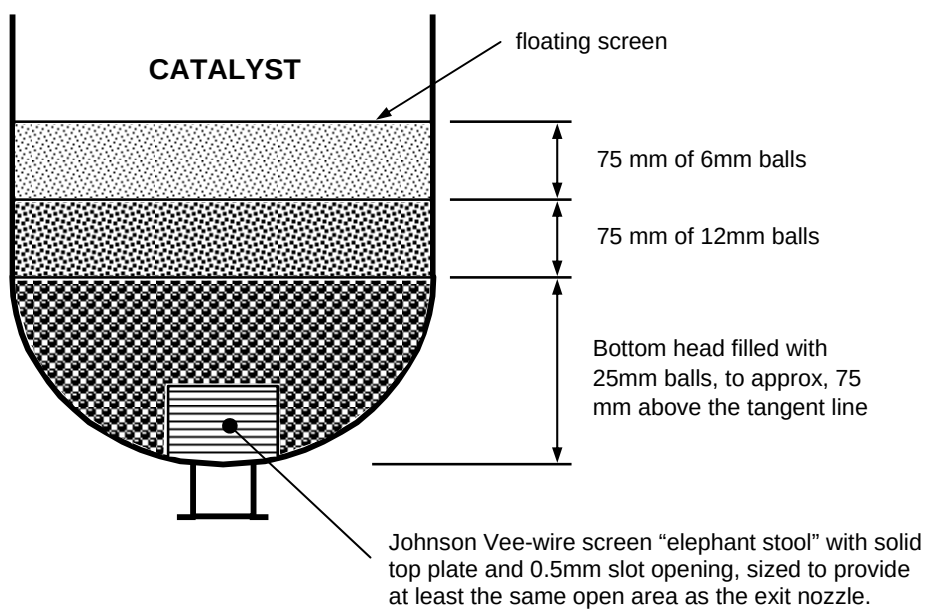


Figure 3. Bed support detail



III. Putting a Reactor On-Stream

Whether putting a reactor on-stream for the first time after filling with new catalyst, or after having been regenerated (and/or in standby following regeneration), the same procedure applies (remark: a preloading by exchange of Nitrogen with Propylene vapor first before charging liquid propylene can be applied instead of direct dosing of liquid propylene).

1. Pressurize the vessel with nitrogen to a pressure approx. 1 bar higher than the vapor pressure of propylene at operating temperature. This is to prevent flashing of propylene liquid into vapor when introducing liquid into the vessel. Do not pressurize too rapidly, however, or the catalyst bed can be disturbed; recommended maximum rate of pressurization is 1 bar per minute.
2. Introduce liquid propylene from the bottom of the vessel at a controlled rate such that the linear velocity (rate of rise of the liquid level inside the bed) is preferably between 1 meter per minute and 2 meters per minute. It is important not to fill too slowly in order that the heat of adsorption of propylene on the catalyst surface is dissipated by transfer of the heat into the liquid propylene. And it is important not to fill too fast in order to avoid flotation of the catalyst bed.
3. The pressure inside the vessel should be monitored. Gas may be bled out as necessary to allow the vessel to fill, but sufficient pressure maintained in order to prevent the propylene from vaporizing.
4. Once the vessel has been completely filled with liquid, a minimum flow of at least 30% of the design rate should be established through the bed, and then rates can be gradually brought up to operating requirements over a reasonable period of time (at least 1 hour).

IV. Regeneration Procedure

Typically the design cycle length of R3-17RED is in the range of 1 – 12 weeks based on design feed compositions. Actual feed compositions may differ from design, and may vary over time. In addition, direct analysis of CO at < 1 ppm in propylene is quite challenging. Therefore it is difficult to predict precisely the best time to regenerate the bed. Correlating cycle length of the CO-removal beds with consumption of polymerization catalyst (i.e. “mileage”) is probably the best way to judge when to switch and regenerate the spent bed. The procedure for the regeneration is as follows.

1. Isolate the vessel to be regenerated; this may involve insertion of pancake blinds as well as closing of the isolation block valves.
2. Drain the vessel by pressuring or pumping out until the vessel is empty of liquid propylene.
3. Purge with nitrogen at ambient temperature for at least 8 hours, to remove most of the remaining liquid propylene from the pores of the catalyst. This purge step should be done with a gas flow of at least 300 Nm³/hr per cubic meter of bed (GHSV = 300 hr⁻¹)^A; this nitrogen flow should be maintained throughout the subsequent steps as well. Initially the purging should be done with a high backpressure of at least 1 bar above the bed pressure, to retard the rate of vaporization of propylene within the pores of the catalyst; still, some sub-cooling of the bed may occur during this step due to the latent heat of vaporization of the olefin. Gradually decrease the pressure, with an eye on bed temperatures, and continue purging as long as the hydrocarbon level in the purge gas is dropping sharply (this can be checked via GC or portable gas monitor).
4. Begin heating with nitrogen, again with a gas flow of at least 300 Nm³/hr per cubic meter of bed. A minimal backpressure (1 bar or less) is advised for this step and the subsequent steps. Start with nitrogen at ambient temperature and gradually ramp up the temperature at a rate of 50 °C / hr. Do not exceed this ramp rate in order to avoid excess thermal stress on the catalyst.
5. Continue increasing the nitrogen temperature until the gas temperature entering the reactor is at a level to ensure a bed temperature of between 200-220°C; then hold the gas temperature at this temperature and heat the complete bed to this level. The bed is now ready for the oxidative step (from fifth regeneration onwards).
6. In the first four regenerations, a treatment equivalent to 6 hours N₂ at a GHSV of 300 hr⁻¹, should be carried out, without any dosage of Oxygen. Then proceed to step 13.
7. In the fifth or any regeneration thereafter, a treatment equivalent to 6 hours with 1300 to 1500 ppm-vol of O₂ in N₂ at a GHSV of 300 hr⁻¹, should be carried out. (Hint: if the N₂ system can only achieve e.g. a GHSV of 200 hr⁻¹, the treatment should still be with 1300 to 1500 ppm-vol of O₂, but with a longer duration of 9 hours). Do not dose more than 3 NL of Oxygen per liter of catalyst during the regeneration. Per 1000kg of catalyst R3-17RED about 9500 NL air are for a full regeneration procedure (equivalent to 1990 NL O₂).

^A GHSV = Gas hourly space velocity [Nlit Gas / hour / lit catalyst]

8. Begin adding air into the nitrogen at a rate that results in an oxygen concentration of 1300 to 1500 ppm-vol entering the reactor.
9. Maintain the flow of gas with 1300 to 1500 ppm-vol of oxygen at **GHSV = 300 hr⁻¹** and 200-220°C bed temperature, for a period of at least 6 hours (for 10 m³ catalyst). During this step, the CO removed during the previous cycle will be rejected from the bed in the form of CO₂. Additionally, any propylene remaining on the surface of the catalyst after the purge (Step 3 above) will be oxidized to CO₂ and water.
10. If possible, monitor the effluent gas for hydrocarbon, O₂, CO₂ and/or H₂O. Such measurements may help confirm the progress of the regeneration.
11. Now the bed must be purged of oxygen and cooled. Stop the air flow. Maintain nitrogen flow and 200-220°C bed temperature for 4 hours to achieve removal of most of the oxygen from the catalyst pores, then gradually decrease the gas temperature (max. ramp rate of 50°C / hr) until the nitrogen temperature is down to 25°C, then continue cooling with N₂ at 25°C until the entire bed has been cooled to below 50°C.
12. Final check of the O₂ content of the purge gas with an O₂ analyzer should be made to ensure that the bed has been effectively purged of oxygen (O₂ level of < 1 ppm).
13. The regeneration procedure is now completed and the bed can be placed in standby. A positive nitrogen pressure must be maintained, to prevent the ingress of air, until the bed is placed back in service.

V. Shut-down and de-commissioning of a Reactor

Shut-down for temporary de-commissioning

If the reactor, containing the PuriStar[®] R 3-17RED bed needs to be shut down for only a few hours, it can be kept under propylene. However, if the shut-down is expected to last twelve (12) hours or more, it is recommended to release the process liquid from the reactor vessel in order to not accumulate any impurities which might be formed by slow chemical reactions between the PuriStar[®] R 3-17RED catalyst and the stagnant propylene liquid, causing



The Chemical Company

oligomerization and polymerization reactions. It is recommended to keep purge the reactor with an inert gas, such as nitrogen.

It is recommended to drain, pressure or pump out the process liquid and then to purge with nitrogen at ambient temperature and pressure before blocking in the reactor vessels by valves. The unit should be kept under a dry blanket of inert gas to avoid moisture pick-up and the need for re-drying before bringing the purification reactor back on-stream.

Shut-down for permanent de-commissioning

If the PuriStar® R 3-17RED bed has reached the end of its lifetime, the reactor vessel needs to be shut down and de-commissioned in order to remove the catalyst bed from the reactor vessel. Again, it is necessary to release the process liquid from the reactor vessel as described above for a temporary shut-down. The partially reduced catalyst has to be re-oxidized before the reactor can be opened and the catalyst can be exposed to air. Prior to opening the reactor vessel it must be ensured that the reactor does not contain any flammable atmosphere. Residues of vaporized hydrocarbons, which could spontaneously ignite if contacted with the atmospheric oxygen, must be removed by blow-drying the catalyst bed with ambient-temperature nitrogen at a recommended **GHSV of 300 hr⁻¹**. During this procedure the hydrocarbon content of the nitrogen shall be analyzed at the reactor outlet to ensure the absence of any hydrocarbon residues to levels below the explosion limit.

As the PuriStar® R 3-17RED bed has been operated in its partially reduced form and may have retained much of its reduction degree, it possesses reactivity when exposed to air. One option to remove its reactivity is to oxidize the bed with air diluted in nitrogen after carefully removing residual hydrocarbons to below the explosion limits. This can be performed by applying a flow of 1% Oxygen in Nitrogen (air mixed with Nitrogen) at a bed temperature of 160degC to avoid any over-temperatures above 230degC caused by exothermic reaction.



The Chemical Company

A suitable technique for passivating the catalyst is to flood the vessel with water until the catalyst is completely covered. Thereafter, the catalyst shall be released through the catalyst-unloading nozzle at the bottom of the vessel into flow-bins or empty catalyst drums. In these drums again the catalyst shall be kept under water. In this case the oxygen dissolves slowly into the water and re-oxidizes the catalyst without significant temperature increase.

We recommend NOT contacting the catalyst with steam or with combinations of steam and air. With steam the catalyst can undergo hydrothermal degradation, ending up in the formation of a concrete composite of the catalyst tablets, which could then only be removed from the reactor by massive mechanical treatment (e.g. pneumatic hammer or explosives).

VI. Unloading and disposal of spent PuriStar® R 3-17RED

After carefully re-oxidizing and then removing the hydrocarbon hold-up of the reactor vessel and an eventual passivation, the spent PuriStar® R 3-17RED catalyst can then be safely removed either by allowing it to drop out of a nozzle at the reactor bottom, or by vacuuming it out of the reactor top with an appropriate vacuum apparatus.

Flooding with water can make the catalyst removal more difficult, however, because if left under water for a while the PuriStar® R 3-17RED tablets tend to stick together and may not freely flow out of the vessel by gravity alone. In this case some "rodding out" may be required to assist in removing the catalyst, if unloading from the bottom of the vessel. Due to the requirement of special activation of the catalyst an unloaded catalyst cannot be reused.

Prior to making arrangements for disposal or reclamation of spent PuriStar® R 3-17RED, the EPA TCLP test should be applied to determine the material's classification, i.e. hazardous or non-hazardous. Up to now, in all cases where the TCLP has been applied with arsenic levels up to 1 wt%, the material has been classified non-hazardous (it "passes" the TCLP). For the reactor service and catalyst disposal we recommend different companies depending on the region, where the plant site is located. For additional information about disposal or reclamation



The Chemical Company

of spent catalysts, or current contacts to firms who can assist in the placement of spent catalysts, please contact your BASF representative or the regional BASF Catalysts Centre.

The data contained in this publication are based on our current knowledge and experience. In view of the many factors that may affect processing and application of our product, these data do not relieve processors from carrying out their own investigations and tests; neither do these data imply any guarantee of certain properties, nor the suitability of the product for a specific purpose. Any descriptions, drawings, photographs, data, proportions, weights etc. given herein may change without prior information and do not constitute the agreed contractual quality of the product. It is the responsibility of the recipient of our products to ensure that any proprietary rights and existing laws and legislation are observed (23.3.2012).