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Technical Guideline

H0-14 S3

Some Indications on Handling and Special Operation

Loading / Activation / Start-up and Shutdown / Regeneration / Unloading

General

The following guidelines explain how to handle H0-14. This document covers the following points:

1) Loading of the catalyst
2) Catalyst Activation
3) Start-up and Shut down
4) Regeneration of Catalyst
5) Unloading of the Catalyst

This document will not address questions regarding toxicological information. For this type of information please refer to the respective safety data sheet (SDS).

This document addresses only certain aspects of safe handling and operation of H0-14. Further details need to be developed and reviewed before or during a process hazard analysis (PHA).

The local safety regulations must be strictly observed when handling BASF Catalyst H0-14.

To minimize Palladium (Pd) losses during all operations indicated here, please refer to the respective document on “Maximizing PGM Recovery” (BF-10723).

Safety

In the following, only some aspects regarding normal operation as well as special operations will be described and the user made aware of.

Normal Operation

During normal operation (hydrogenation step) no special risks concerning process safety have been identified or experienced. The typical considerations for leakage of LPG type streams as well as potential pressure build-up under higher temperatures need to be considered.

The presence of hydrogen (H_2) in the feed stream must be properly limited (e.g. by interlocks). Hydrogen in higher concentrations can lead to the hydrogenation of any propylene present, which is an exothermic reaction. Thus, it is also not allowed to pressurize the vessel with hydrogen or hydrogen containing gases before filling the vessel with propylene.

Reduction

During the reduction of palladium oxide (PdO) containing catalysts like H0-14 no special risks concerning process safety have been identified or experienced. The typical considerations for leakage of H_2 containing gases need to be considered. Also, it needs to be adhered to the maximum reduction temperatures indicated to avoid damaging the Pd crystallites formed during reduction.

Filling

Even if the pressure set on the vessel before filling is sufficient to keep the hydrocarbon (here propylene or propylene/propane mixtures) in the liquid form, it cannot be excluded that very low temperatures at the inlet of the liquid can be observed. This is due to the mixing of vapor hydrocarbon and nitrogen as present in the vessel, which can achieve much lower temperatures as would be expected from the respective vapor pressure curve of the respective hydrocarbon. This might need to be considered in the selection of the material of construction of the vessel and the control valve in the off-gas system (see also explanations on the filling step).

Regeneration

Regeneration aims at removing any carbonaceous components (e.g. oligomers or polymers formed and present on and in the catalyst) by oxidation with air. To control any significant increase in

temperature, which could lead to damage to the catalyst or the vessel, proper control of the amount of air (e.g. by interlocks) added needs to be always ensured. It also needs to be safely ensured that no hydrogen can mix with the air added or ingress into the vessel under regeneration. To properly monitor the progress of the regeneration sufficient temperature measurements, need to be installed in the bed which are typically interlocked with the air and the heat added to the gas entering the vessel.

Handling of the catalyst

In the following information is provided on how to handle H0-14 in different situations. The guide covers the following points:

1) Loading of the catalyst
2) Catalyst Activation /Start-up
3) Reduction of the Catalyst
4) Regeneration of the Catalyst
5) Unloading of the Catalyst

1) Loading of the Catalyst

Loading of the catalyst into a vessel should be consistent with the following guidelines.

1. Before the catalyst is loaded, the vessel should be cleaned, leak-tested and inspected. The inside walls and any internals must be clean. Especially any rust formed during exposure to humid air or during any pressure vessel testing needs to be removed. The condition of the vessel should be documented with respect to corrosion and wall thickness.
2. Before the catalyst is loaded, it needs to be checked that all parts which need to be loaded into the vessel (e.g. the nets to be installed between the catalyst and the layer of inert balls on top of the catalysts) are available and in good condition.
3. Before the catalyst is loaded, the availability of all equipment needed to load the catalyst, like hoppers, chute or filling pipe, crane, forklifts and experienced personnel to do the loading need to be ensured.
4. Before the catalyst is loaded, the drums in which the catalyst is supplied should be checked for any possible damage suffered in transit, if not already checked during reception of the good.
5. It is recommended to write a loading protocol showing the number of drums and the catalyst weight loaded into the vessel, including the catalyst's lot numbers. In addition, the bed height, the catalyst volume and the loaded density of the charged catalyst should be reported. The time needed for loading the catalyst can also be documented to allow better planning for future catalyst change-outs. The same data should be reported for the inert balls
6. Before charging the catalyst into 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 the leveling of the bed and will also assist in getting the correct quantities of materials loaded.
7. The installation of the thermocouples depends on the configuration chosen. If possible, all thermocouples should be installed before loading any material into the vessel. Else the installation of the thermocouples follows the progress of the loading.
8. Suitable bed support must be installed before catalyst loading begins. See Figures 1 to 3 for a typical bed support design. All support balls filled into the vessel must be levelled before adding the catalyst.
9. The catalyst can be charged directly from drums or from a loading hopper.
10. BASF catalyst H0-14 adsorbs moisture from the air. Therefore, the drums should be kept closed and opened only shortly before filling the catalyst. Care must be taken to protect the catalyst from rain.

Figure 1 – Overview of Reactor Loading

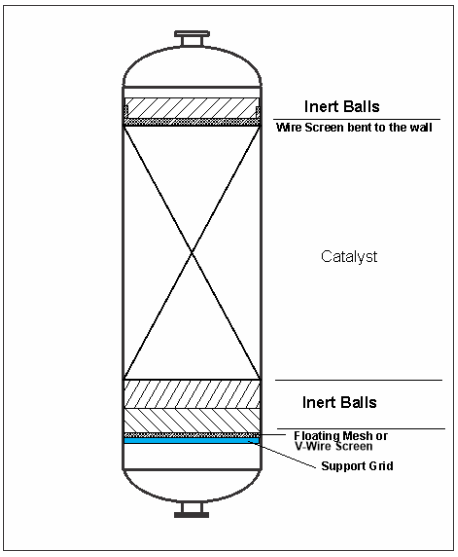


Figure 2 – Top Inert Ball Layers

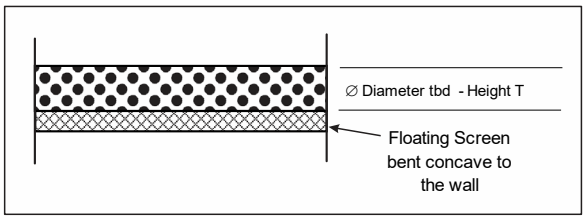
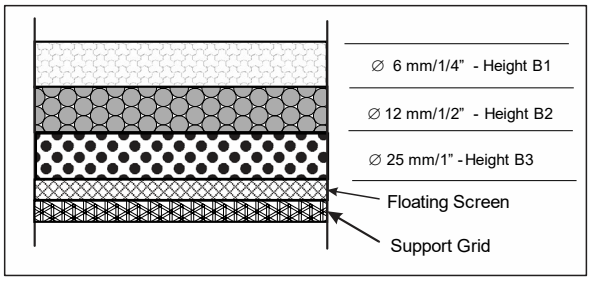


Figure 3 – Bottom Inert Ball Layers



11. Catalyst loading should be done steadily and without any longer interruption. Once the catalyst and the inert balls are loaded into the vessel, the reactor should be closed and the vessel sealed with nitrogen.
12. The catalyst must not be allowed to free-fall more than 1 meter / 3 feet. The free-fall can be controlled by loading through a funnel with attached canvas sock/hose (hence "sock-loading").
13. Pinching down on the end of the hose to always keep the hose full of catalyst during filling is advised. The end of the sock is guided to avoid discharge of the catalyst at the same place. By assuring good distribution of the catalyst, an even flow distribution across the catalyst bed is ensured, resulting in high effectiveness of the catalyst bed.
14. Periodically the sock must be shortened to avoid kinking during the filling.
15. If personnel must enter the vessel during the filling or at any time after the catalyst loading phase commenced, boards should be placed on top of the catalyst for the worker to stand on. Treading directly on the catalyst should be avoided as this can lead to attrition and the creation of fines in the bed. It needs always to be ensured that all boards or planks are accounted for and that any plank or board taken into the vessel is removed from there to avoid channeling in the bed.
16. Personnel entering the vessel must wear the proper personnel protective equipment (PPE) as indicated in the respective SDS.
17. After all catalyst has been loaded into the vessel, the bed must be leveled.
18. Finally, the hold-down layer of inert balls (see Figure 2) must be put in and leveled. The hold-down layer is put onto a net to avoid the inert balls, which are typically much heavier than the catalyst, leading to crushing of the catalyst. To avoid inert balls moving along the wall into the catalyst bed, the net must be bent concave to the wall.
19. After filling, the vessel should be tightly sealed until it is put into service. To have the vessel ready for the next steps it is recommended exchanging the atmosphere in the vessel from air to nitrogen and to keep the vessel under a slight N_2 pressure of e.g. 0.5 bar (7 psi) above atmosphere.

2) Reduction

To give the catalyst its full activity and selectivity, a reduction of the catalyst is required before the first start up and after each regeneration in case a regeneration is done.

By reducing the catalyst, the noble metal oxide, which is present on the freshly delivered and the regenerated catalyst, will be transformed to the respective noble metal:

$$\mathbf{PdO + H_2 \Rightarrow Pd + H_2O}$$

The reduction is done by exposing the catalyst to hydrogen at temperatures of about 120°C / 250 °F. Hydrogen is typically diluted into an inert gas stream like nitrogen.

Due to the low content of Pd on H0-14, the amount of water formed is small and is typically limited to the initial part of the reduction.

After filling in the catalyst, the reactor must be blanked off from the air (oxygen) by nitrogen. The reactor should be heated up with an inert gas (like nitrogen) to 120°C / 250°F with a temperature rise of max. 50°C / 90°F per hour.

As soon as the temperature at the outlet of the reactor reaches 120°C / 250°F, H_2 is added slowly to the inert gas stream. The observed temperature increase is marginal to only a few degrees centigrade (maximum temperature 130°C / 265°F).

After 10 - 12 hours the reduction is complete. The hydrogen addition is stopped, and the reactor is cooled down with the inert gas stream to the normal operating temperature or ambient temperature depending on the next steps foreseen.

Until the reactor is required for service, it should be kept under an inert gas atmosphere of about 2 bar (30 psi).

A summary table of special operations can be found at the end of this document.

3) Putting a Vessel on Stream

Filling the Vessel with Liquid

Whether putting a vessel on-stream for the 1st time after filling with fresh catalyst and reduction or after having been regenerated (and/or in stand-by following regeneration) and reduction, the same procedure applies.

The material used for filling of the vessel leading to the wetting of the catalyst can be either done with feedstock (as specified) or product. Both are considered safe enough in the absence of hydrogen to allow for proper soaking of the catalyst.

1. Pressurize the vessel with nitrogen to a pressure approx. 1 bar / 14.5 psi higher than the vapor pressure of propylene at operating temperature. Figure 4 provides a typical vapor pressure curve for propylene only. In case of use of mixtures of propylene with propane or other hydrocarbons are treated, please refer to the respective p,T diagram. This is to minimize flashing of propylene liquid into vapor when introducing liquid into the vessel. Do not pressurize too fast however as else the catalyst bed can be disturbed. The recommended maximum rate of pressurization is 1 bar per minute.

Figure 4a – Vapor Pressure Curve of Propylene in SI Units

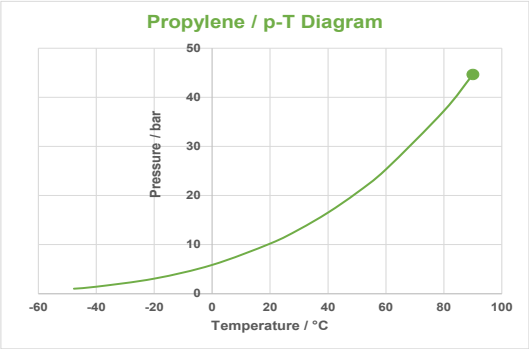
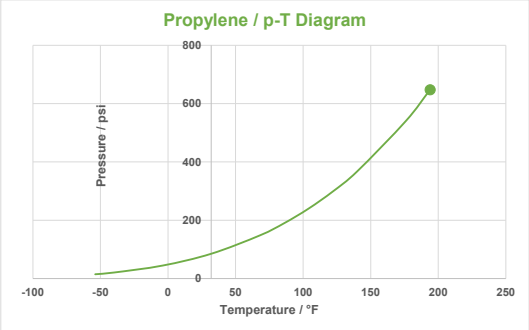


Figure 4b – p,T Diagram for Propylene in Imperial Units



2. Introduce liquid propylene from the bottom of the vessel at a controlled rate such that the linear velocity (rate of rise of liquid inside the bed) is preferably between 1 and 2 meters per minute. It is important not to fill too slowly in order that any heat of adsorption of propylene on the catalyst is dissipated by transfer of the heat into the liquid propylene. And it is important not to fill too fast to avoid fluidization of the catalyst bed.
3. The pressure inside the vessel should be monitored. Gas will be bled to off-gas as necessary to allow the vessel to fill, but sufficient pressure should be maintained to prevent the propylene from vaporizing.
4. The end of the filling of the vessel is typically determined by the freezing of the valve controlling the gas flow to off-gas. The freezing (ice deposition) is sign of flashing of the propylene in the valve. Alternatively, the filling needs to be monitored by measuring the liquid level in the vessel.

Start-Up

Once the vessel is filled with propylene, the reactor can be started up. Before starting up, the handling of off-spec material. Off-spec material in this case refers to a product stream which has too high a MAPD content.

This start-up can be done as follows:

- Start feeding in fresh H_2 (as specified) and this at a ratio of 1,2 – 1,3 to the ratio as defined during normal operation (assuming normal MAPD content). This will lead potentially to over-hydrogenation but at the same time assures that the hydrogenation starts.

- Ramp the feed flow rate to normal rates while adjusting the H_2 flow rate.

- Evaluate the product coming from the vessel for MAPD and propane content.

- Once the product fulfills the specification for MAPD, line the system up towards the downstream unit.

- In case the product coming from the hydrogenation is off-spec, it is required first to check on analytics and then on the composition of the feed. The case being the hydrogen to MAPD ratio needs to be adjusted.

- In case the vessel is operated at a temperature higher than the feed temperature, adjust first the temperature to this level before adding H_2 to the stream.

Shutdown

When shutting down the unit, the aim is to achieve an overall safe state. This is achieved by first cutting hydrogen, then the feed. The following steps are recommended:

- Bring the present feed rate (and hydrogen) down to 1/3 of the design value in 2 or 3 steps.

- Reroute the product to battery limits.

- Stop the hydrogen flow and block it in

- After 10 – 20 minutes, stop the feed

At this time, the system can be expected to be in a safe state. In case any temperature increase is observed over the catalyst bed, it is necessary to continue liquid flow (the case being by recycling) over this bed without hydrogen addition, until the temperature increase has died down.

In case the system must be opened, it will be required to drain the vessel to battery limits, to depressurize the system and exchange the atmosphere to a safe atmosphere.

4) Regeneration

For the typical applications in which H0-14 is used, H0-14 exhibits high robustness and a long lifetime.

During the lifetime or during exceptional conditions (like when higher amounts of multiple unsaturated components come in contact with the catalyst), the H0-14 may experience slow deactivation through deposition of coke on the active sites of the catalyst and by blocking part of the pore structure of the catalyst.

In cases, it is worthwhile trying to extend the life of the catalyst, a regeneration step to recover the original level of activity can be adopted. The regeneration is done once the end of run (EOR) conditions have been achieved. Through regeneration, the coke (which is a composite of different hydrocarbons) will be burnt off with air, forming carbon dioxide and water according to the following general equation:

$$\mathbf{C_xH_y + (x+y/4)\ O_2 \Rightarrow x\ CO_2 + y/2\ H_2O}$$

Regeneration is carried out at temperatures between 400 to 450 °C / 750°F to 840°F. To control the temperature of the catalyst bed, the regeneration is carried out with an inert gas/air mixture. The inert gas is typically nitrogen. The use of steam is also possible, if steam is only used at temperatures beyond 150°C / 300°F to avoid any condensation of water in the pore system of the catalyst.

Regeneration consists in general of the following steps, described in detail for the regeneration with nitrogen. The respective flow rates can be found in the table at the end of the document:

a. Prior to regeneration, the process stream is blocked out and the reactor is separated from the rest of the plant. After blocking in, the reactor is drained and slowly depressurized.

b. **“Heating”:** The reactor is heated to 150°C / 300°F with nitrogen at a maximum rate of 40°C / 70°F per hour.

c. **"Stripping":** The flow rate of the nitrogen is then increased stepwise up to the maximum flow rate indicated and the reactor heated up to 250°C / 480°F at a maximum rate of 30°C / 50°F per hour. During this step any hydrocarbon, which can be vaporized, will be removed with the hot gas. By doing this the total amount of heat generated during the oxidation steps can be reduced.

d. **"Pre-oxidation":** When the temperature has reached 250°C / 480°F, the injection of the minimum air rate is started. The temperature is kept at this level for 1 to 2 hours (depending on whether the passing of a temperature wave in the respective reactor is observed or not).

e. **"Heating":** In this step the temperature is increased to 400°C / 750°F at a maximum rate of 30°C (50°F) per hour. In case a temperature increase (typically in form of a wave moving through the bed) is observed during this temperature increase, the temperature increase will be stopped until the temperature indicators have levelled down again.

f. **"Burning":** Once the temperature of 400°C / 750°F has been reached and no further temperature wave is observed in the reactor, the air rate will be increased stepwise up to the maximum flow rate, without however exceeding 450°C / 840°F in the reactor.

g. **"Finish Burning":** Once no temperature rise is observed any more, the inlet temperature is increased to 430°C / 800°F (if possible) to promote complete removal of carbon. Addition of air is continued until less than 500 ppm by volume of CO_2 is analyzed at the reactor outlet. The analysis for CO_2 can be done with an analyzer installed dedicatedly in the off-gas line or by taking gas samples and analyzing them in the lab or with the help of length-of-stain testing tubes. The temperature shouldn't exceeding 450°C (840°F) in the reactor.

h. **"Cooling":** The air is then switched off and the reactor slowly cooled down with nitrogen until the required temperature for the reduction (120°C, 250°F) has been reached. At this point the reduction is carried out as indicated under the previous point.

A summary table of special operations can be found at the end of this document.

5) Unloading of the Catalyst

Catalyst, which needs to be unloaded, can contain hydrocarbons or other flammable components, which when brought into contact with air can start reacting and lead to a temperature increase and formation of smoke. Please note that the reduced Pd present on the catalyst will react with oxygen to form the respective oxide. However, due to the small content present in the catalyst, this reaction will only lead to temperature increases of a few °C / °F.

It is strongly recommended that before unloading the catalyst, the bed is at least stripped with nitrogen at a temperature of 120°C. To further minimize any hazard during unloading, the nitrogen present in the vessel is slowly exchanged for air. In case any temperature increase would occur, the complete nitrogen blanketing is restored until all temperatures have died down. Only once no temperature increase can be detected after replacement by all nitrogen with air, can the vessel be opened. The catalyst can be discharged by using industrial vacuum cleaner equipment and shipped safely to a metal reclaimer to recover the Palladium.

Nitrogen Procedure

- Catalyst Volume: 10 m^3

- For converting the N_2 amounts indicated in Nm^3/h to mass flows, please multiply the indicated values with 1,25 kg/Nm^3 or 20.0 lb/cuft (once converted into cuft)

- For converting the indicated Nm^3/h to scft/h please multiply with 35.8 $scft/Nm^3$

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Step	Gas components	Flow Rate Nm³/h	Temperature °C	Temperature Increase °C/hr	Time at Temperature Hours	Total Duration Days
Reduction						1
Heating	N2	1 000	Up to 120	Max. 50	-	
Reducing	N2 + H2	1 000 + 300	120 (max- 150)	-	10-12	
Cooling	N2	1 000	-	-	-	
Regeneration						2-3
Heating	N2	1 000	up to 150	max. 40	-	
Stripping	N2	1 300 – 4 000	up to 250	-	8 - 10	
Pre-Oxidation	Air + N2	40 + 4 000	250	-	1-2	
Heating	N2	40 + 4 000	up to 400	max. 30	-	
Burning	Air +N2	40 – 400 4 000	400-450	-	4 - 8	Air + N2
Cooling*	N2	4 000	down to 120	-	-	

* This step should normally be followed directly by the reduction of the catalyst, except when the catalyst is unloaded.

The pressure should be chosen so that the off gases can be directed to battery limits (max. 5 bara / 70 psia)

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BASF is a leading global manufacturer of catalysts for the chemical industry, with solutions across the chemical value chain. The business comprises chemical catalysts and adsorbents and custom catalysts. Priority is given to developing new and improved products that enable the chemical industry transformation to net-zero emissions.

BASF's chemical catalysts and adsorbents business is part of the company's Performance Chemicals division. The division's portfolio also includes refinery catalysts, fuel and lubricant solutions, as well as oilfield chemicals and mining solutions. Customers from a variety of industries including Chemicals, Plastics, Consumer Goods, Energy & Resources and Automotive & Transportation benefit from our innovative solutions.

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BASF-10637 Rev. 08/25