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## **Question 10: Does hydrotreated product recycle count the same as fresh virgin feed for the catalyst break-in period?**

**BODOLUS** (CVR Energy)

Yes, recycled product is generally acceptable during the break-in; but as we have discussed earlier, perhaps not all recycled product is created equal. ULSD recycled product is going to be a lot better than an ultra low sulfur gasoline recycled product that may have the residual olefins in it. And again, synthetic crudes, if fresh virgin feed or from a synthetic crude, may or may not have residual issues associated with olefins as a result of whatever production process they went through.

Generally, a break-in period is very dependent upon the catalyst type in the intended service; so, it changes a little with each unit. To reiterate again, it is important to have a good relationship with your catalyst vendor. Ask specifically what the vendor wants to see in terms of unit start-up procedures and feed specs. You need to gravitate back to the actual specifications of the feed rather than just to a catch-all term like, "Oh, okay, it is straight run material." Take a look at the boiling point constraints if there is an endpoint limit or measurement of olefins. You want little or no olefins in this start-up material or break-in material. During the break-in, you need to monitor bed performance and keep track of the bed  $\Psi$ s as best you can; and if you find those going off the tracks, then implement some corrective action.

There are a wide range of catalysts and catalyst prep options available. Not only is it important to select the base catalyst you want, but you have a lot of pretreatment options. The traditional oxide form can be loaded in a regular air atmosphere, but that will take the longest time in a post-turnaround interval to get you back up and running again where you have to sulfide that catalyst, in situ. If presulfided, you can shave off a little time. Now of course, there is preactivated material as well, which has a more limited break-in period. However often, depending on the catalyst, you will still have to restrict the number of cracked stocks. Some of the pretreatment vendors now believe that they have kind of a load-and-go type of catalyst which provides some cracked stock protection during the break-in period.

The key ideas this afternoon's Principles & Practice session is going to address are a lot of these turnaround issues; because as we all know, pressures from management to shorten the break-in period after a turnaround can be significant, crushing, demanding, whatever you would want to say. As you get towards that very end of the turnaround, everyone is tired. You see the taillights of everyone leaving the site, and the last step to do is this break-in period. Everyone wants to know why it cannot happen in a couple of hours. So there is a lot of pressure at that point in the turnaround experience. The P&P session this afternoon should be good for you all to attend to learn more about this subject.



## Does Hydrotreated Recycle Count as "Fresh Virgin Feed" for the Catalyst Break-In Period?

- Generally, Recycled Product is Acceptable for Break-in Period... BUT
  - Not all recycle is created equal – Recycle ULSD vs ULSG
  - With Synthetic Crudes even "Fresh Virgin Feed" may have issues
  - Break-in very dependent upon Catalyst Type and Intended Service
  
- Focus on the Feed Composition and Bed Temperature Limits
  - Have Catalyst Vendor assist with Start-Up Procedures and Feed Specs
  - Constraints on Boiling Point (< 700 Deg F EP) and little or no Olefins
  - Monitor Bed Performance and Moderate Delta T as able
  
- Close Alliance with Catalyst Vendor and T/A Planners BEFORE START-UP
  - Wide Range of Catalyst Pre-Treatment Options to Select From:
    - Traditional Oxide Form – Atmospheric Load / Sulfide and Activate In-Situ
    - PreSulfided Form – May Need Inert Loading / Activation Step
    - PreActivated Form - May Need Inert Loading / Limited Cracked Stocks
    - PreConditioned Form – Load and Go / Provides Cracked Stock Protection

***Pressure from Management to shorten Break-In Period after a Turn Around can be Significant!***



**ANDREW LAYTON** (KBC Advanced Technologies, Inc.)

If it is hydrocracker start-up, remember that recycle has had the sulfur and nitrogen removed. You can run into trouble if you do not realize that the nitrogen in the total feed is dropping, which can give you a temperature runaway start-up. So to some extent, recycle is not the same as virgin feed because the

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nitrogen has been partly removed, which can make the hydrocracker catalyst overactive at start-up. This is not such a significant consideration for normal hydrotreating catalysts without zeolite content.

**STEPHEN PERRY** (Motiva Enterprises)

I am not sure if I heard it or not, so to reiterate: If you are going to use recycle during the break-in period, make sure you flush the catalyst fines out to tankage before closing the recycle loop to the feed drum.

**BODOLUS** (CVR Energy)

Yes, that is a good point. You want to flush the catalyst fines that first couple of hours or until you see the product run clear, yes, and then go to recycle mode. Good point.

**BODOLUS** (CVR Energy)

Generally, the recycled product of a hydrotreater is acceptable feed during the break-in period, but the better criteria for what to use depends on the process, the compositional details of the feed, and the catalyst type. Due to the highly active state of the catalyst during break-in, it is the exotherm generated in the bed that needs to be monitored, controlled and moderated. Key input in what feed slate and break-in period to use should be provided by the catalyst vendor as there are many specific issues involved.

The ability to use recycle material also depend on the type of hydrotreating process is involved. Recycled ULSG has appreciable residual olefins and may not be appropriate as the initial start-up material. For recycled products that may have residual exothermic activity, the catalyst vendor can provide guidelines for acceptable bed temperature limits.

Care should also be paid to determining the origin of the “fresh virgin feed”. Just because the feed was derived as straight run from crude distillation may not automatically mean that it is acceptable as a start-up feed. As various “synthetic crudes” appear on the market, it is difficult to know the previous processing history of the crude fractions. Focus should be on the specific parameters the catalyst vendor requires to assure successful start-up. Start-up feed selection criteria should be based on physical and chemical parameters such as material endpoint, olefins content or aromatics constituents. Unless otherwise specified, break-in feeds for diesel units should have an endpoint less than 700°F and very low or no measurable olefins or diolefins.

Following a catalyst change-out, total time from warm-up to on-specification can vary dramatically depending upon the catalyst type and state. Catalysts can be provided in oxide form, presulfided, preactivated, or preconditioned (for cracked feed protection). Selection of the catalyst preprocessing can shorten the break-in time, but each selection has an optimal time line and preparation costs. Working with the turnaround planners well before the change-out can help establish and communicate options and alternatives.

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Pressure from refinery management to shorten conditioning period after a turnaround can be significant. Delays experienced early in the maintenance process may compress the originally envisioned start-up window. Note that specific steps that can be taken to minimize overall downtime are covered in this meeting with a Principles & Practice session.

**ERJA RAUTIAINEN** and **STEVE MAYO** (Albemarle Corporation)

When giving an answer to this question we have assumed that the break-in period is the period directly after the catalyst presulfiding has been completed and the fresh feed is taken in.

After the catalyst presulfiding has been completed it is advised not to feed cracked stock during the first three days of operation. Hydrotreated product would meet this requirement; however, there are other concerns using hydrotreated product for catalyst break-in. One problem is the typically low sulfur content of the material. A minimum amount of H<sub>2</sub>S is needed to ensure complete sulfidation is maintained on a freshly sulfided catalyst. Too low H<sub>2</sub>S partial pressure may cause metal sulfides to transform into an inactive metal state, which is very difficult to transform back to a sulfide. This problem could be overcome by injection of a sulfur (S) spiking agent, such as DMDS, to the feed. The exact amount of sulfur required can be calculated with the help of phase diagrams, but we typically use between 25 ppm and 50 ppm S in the feed.

Another, more difficult to overcome, issue is the lack of coke forming components in a hydrotreated feedstock. While it is desirable to avoid the introduction of high concentrations of coke precursors, de-edging of the hyperactivity of freshly sulfided catalyst necessitates a controlled deposition of coke. Break-in with a hydrotreated product will less easily accomplish the required de-edging of catalyst activity and leave the catalyst susceptible to rapid coke deposition when cracked feedstock is added. The recommended a three-day break-in before cracked feed addition is ineffective because so little activity de-edging will occur with hydrotreated feedstock. If fresh virgin feedstock is not available for the break-in period one solution is to blend a small amount of cracked feedstock with the recirculating hydrotreated product. While not a recommended solution, it may be superior to alternatives for de-edging catalyst activity during the break-in period.

**MEREDITH LANSDOWN** and **BRIAN WATKINS** (Advanced Refining Technologies)

Hydrotreated product recycle can be supplemented for feed during the catalyst break-in period after sulfiding; however, there are several issues that need to be considered when doing so. The initial break-in period is designed so that the catalyst does not see elevated initial temperatures along with materials that could prematurely place a high level of coke down on the catalyst surface. This allows the hyperactive sites on the catalyst that are present just after sulfiding to be tempered in order to prevent this. Use of product recycle has the advantage that the material will be very low in coke precursors present in other stocks which will help prevent rapid coke laydown. It also has the advantage that if this is done to supplement a shortfall in total feed to the unit due to a limited quantity of available straight run stocks, the unit can be maintained at maximum rates, ensuring that good distribution is maintained and minimizing premature fouling.

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The downfall would be if product recycle is the sole source of feed to the unit, then over a short period of time, all of the sulfur will be removed from the feed. This will increase the hydrogen partial pressure at the catalyst surface and could begin to reduce the active metals if H<sub>2</sub>S presence is not maintained to keep the catalyst sulfided. In this case it is recommended that minimum H<sub>2</sub>S levels on the order of 5000 wppm (weight parts per million) are maintained in order to keep the catalyst sulfided. It is also recommended that temperatures no higher than the final sulfiding temperature be used to also minimize any possible reduction or premature coking.

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