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XPRESS: THE FIRST TRUE EX-SITU PRE-SULFIDING PROCESS

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Abstract

TRICAT has introduced the first technology to truly pre-sulfide hydroprocessing catalyst prior to loading the catalyst into the unit. The catalyst is passivated against self-heating, and can be loaded in air into the hydroprocessing unit. Unit start-up is greatly simplified and shortened with no exotherms or water-liberating reactions.

Initial commercial tests have confirmed that catalysts pre-sulfided via this new process, called "XpresS", experience no exotherm during start-up. Laboratory activity testing of the XpresS pre-sulfided catalysts has shown that the pre-sulfided catalyst is as active as catalysts sulfided in-situ using sulfiding chemicals.

Background

Catalysts typically containing Nickel and Molybdenum (NiMo) or Cobalt and Molybdenum (CoMo) dispersed on a carrier composed of alumina, amorphous silica-alumina, or crystalline silica-alumina (zeolites) are used extensively in the refining and petrochemical industry. These catalysts are widely employed in hydrotreating and hydrocracking units to upgrade crude fractions into desired products by removing sulfur and nitrogen; adding hydrogen; and cracking to lighter products.

Tungsten is occasionally used in place of Molybdenum, particularly in hydrocracking catalysts.

As manufactured, the catalyst are prepared with the metals in the oxide form (ie. NiO, CoO, MoO₃ and WO₃). In this form, however, the metals are not active to catalyze the desired reactions. For the catalysts to work as designed, they must first be converted to an active form by reacting the metal oxide with sulfur to form the corresponding metal sulfide. Examples of the sulfiding reactions are shown in Table 1.

The active metal sulfides are typically unstable in air. If exposed, they tend to convert back to metal oxides and metal oxysulfides, releasing heat and sulfur in the form of SO_x. It has proven to be largely impractical to get sulfided catalyst packaged in an inert atmosphere into a reactor without exposure to air.

Historically, the sulfiding reactions are performed in-situ during the hydroprocessing unit start-up. The sulfiding can be performed in either the gaseous or liquid phase, and normally the refiner employs a sulfur-containing "spiking" compound (which decomposes to hydrogen sulfide at sulfiding temperatures) to speed the process. There are several disadvantages to using the in-situ sulfiding method:

- The start-up is exothermic and thus must be undertaken slowly and with great care.
- The sulfiding reaction yields water which must be removed.
- The spiking compounds can be toxic, flammable and/or odorous.

The exothermic nature of the sulfiding reactions pose the greatest concern for the refiner during start-up. In particular, gas-phase sulfiding (which must be employed during hydrocracker start-ups) can be especially troublesome. Because the sulfiding reactions require hydrogen to proceed, there is a concern that the metals can be reduced at high temperatures. If the metals are reduced with hydrogen in the absence of hydrogen sulfide, the sulfiding reactions will not proceed. Agglomeration of the active metals can occur, resulting in severe catalyst damage. The literature suggests that sulfiding reactions are initiated at ~250°F while metals reduction in the presence of hydrogen initiates at ~650°F.¹ While this temperature spread is quite high, exotherms of much greater than 400°F have been observed during gas-phase sulfiding.²

Because of the potential for metals reduction, the inlet sulfiding temperature is held at relatively low temperatures for several hours to allow a temperature wave to pass through the catalyst bed. An excess of H₂S is maintained such that the bed never sees hydrogen alone at conditions that can reduce the metal. The low temperature sulfiding step can continue for as long as 3 days during gas-phase sulfiding in large hydrocracking reactors.

The release of water during sulfiding can also be an area of concern. As water is released, the downstream portion of the catalyst bed is exposed to steam which can deactivate the catalyst if the temperatures are high. Also, special care must be taken to drain the high pressure separator frequently to avoid water carryover.

Even when proper care is taken during sulfiding via this method, the activity of the sulfided catalyst can be poorer than expected due to a number of factors. One of the more common problems is poor distribution of the sulfiding compound during the sulfiding process, resulting in incomplete sulfiding. This will also lead to higher than expected start-of-run temperatures and shorter than expected cycle lengths.

Some improvement in sulfiding has been realized in the past several years with the introduction of "pre-sulfurizing" technologies. In these technologies, the need for a spiking compound is eliminated by coating the catalyst (ex-situ) with molecular sulfur or sulfur-containing compounds.²⁻⁴ The catalyst is not sulfided ex-situ, although some conversion of the metal oxide sites to a metal oxysulfide can occur. The catalyst can then be sulfided in-situ without the need for a spiking compound.

The pre-sulfurized catalysts, however, still require that the exothermic and water-yielding reactions take place in-situ. Since the sulfur is distributed throughout the bed, once sulfiding temperature is reached, the water liberation can be almost immediate. The exotherm can also be quite extreme.² As a result, the start-up of the unit remains time-consuming and subject to upsets.

Xpress Process Development

In 1993, TRICAT introduced the TRICAT Regeneration Process (TRP) to regenerate spent hydroprocessing catalysts in an ebullated (or expanded) bed.⁵ The use of an ebullated bed design provided a significant advantage over older regeneration processes because of the ability of the fluid bed

to carry away the heat released during oxidization of the carbon and sulfur deposited on the catalyst during normal operation.

With the success of the TRP, TRICAT set out to extend the ebullated bed concept toward the exothermic pre-sulfiding reactions. Initial pilot plant testing with a conventional NiMo catalyst showed that sulfur could be distributed uniformly upon the catalyst sample in about 90 minutes with a small exotherm. By contrast, a packed bed of the same catalyst showed uneven sulfur distribution, and a much larger exotherm, across the bed when sulfided under the same conditions.

The amount of sulfur deposited on the catalyst during this initial testing approached stoichiometric levels according to the equations in Table 1. This gave the first indication that no reduction of the metals was occurring at these temperatures.

As expected, catalyst sulfided in these tests was unstable in air. Upon exposure, samples rapidly began to heat, and evolve sulfur. In order to conduct additional testing with the sulfided catalyst, the catalyst was cooled with nitrogen and then submerged in a diesel oil bath. Excess oil was removed from the catalyst by sieving, and the oil was dried from the surface.

The now-passivated catalyst was evaluated for sulfur types. Table 2 shows that nearly all of the sulfur found was in the sulfide form. A single pilot plant activity test conducted by the R&D lab of a major oil company compared the activity of this catalyst with a sample sulfided in-situ in the pilot plant. Their results indicated that the activity of the two samples was equivalent within experimental variation.

More extensive pilot plant testing was also undertaken by another major oil company's R&D lab. This oil company desires to use pre-sulfided catalyst in a specialty chemical application where the feed has negligible sulfur levels. As a result, their test is more sensitive to a poorly sulfided sample because of the inability of the catalyst to continue sulfiding under the typical operating conditions in a hydroprocessing reactor.

In their testing, they evaluated the first order rate constant for their desired conversion reactions. Their activity test was performed with a conventional NiMo catalyst pre-sulfided in TRICAT's pilot plant. In this study, the catalyst was passivated in the reactant for the process. Figure 1 shows

that the activity obtained for the pre-sulfided catalyst during a brief aging study was within the expected activity range they obtained for the same catalyst sulfided in their pilot plant using H₂S.

In scaling up from the pilot plant, the use of oil as a passivation agent appeared to be the most sensitive area. Incomplete removal of the excess oil would leave the sulfided catalyst difficult to handle. Overdrying leaves the catalyst susceptible to self-heating. Several liquids were evaluated which dried more readily than a conventional diesel stream, but the catalyst was still difficult to handle.

To avoid these concerns, TRICAT decided to redirect its efforts towards gas-based passivation agents. Rather than physically coat the catalyst surface to render it inert, TRICAT evaluated methods to passivate the surface through chemical treatment. The objective of these studies was to retain the activity observed for the oil passivated catalyst while also maintaining the stability of the sulfided catalyst at atmospheric conditions.

Considerable testing in the pilot plant yielded a formula which met these goals. Activity testing of catalysts sulfided and passivated using this proprietary formulation was undertaken. Because of the tendency of CoMo catalysts to be more reactive in air, much of the testing was conducted with a fresh CoMo product.

The desulfurization and denitrogenation performance of a CoMo catalyst sulfided and then passivated using this new technique was evaluated extensively. These tests, conducted at an independent laboratory in Europe, compared the activity of TRICAT's pre-sulfided catalyst with a conventionally sulfided catalyst. For conventional in-situ sulfiding, the laboratory employed dioctylpentasulfide (DOPS), a "spiking" agent used in the European market. The laboratory determined that at the conditions employed in their pilot plant, DOPS provided a more uniformly sulfided (and more active) catalyst than did more widely used additives (including DMDS and DMSO). The in-situ sulfiding with DOPS was performed via standard procedures using a gradual heat-up from 300 to 660°F, achieving complete sulfur breakthrough at several temperatures.

Both the in-situ sulfided catalyst and the ex-situ pre-sulfided catalyst prepared by the XpresS method were evaluated with an atmospheric gas oil feed containing 1.2 wt% sulfur and 400 ppm nitrogen. Each catalyst was tested for desulfurization and denitrogenation performance at 600 psig and temperatures ranging from 590 to 700°F. The results are

shown in Figures 2 & 3.

The results show that the activity of the pre-sulfided catalyst is equivalent to the in-situ sulfided catalyst. Additionally, no change in product yields was observed. A brief aging study also showed no adverse aging for the lab pre-sulfided catalyst.

On the basis of these results, TRICAT commissioned Lurgi to design and build a plant in Bitterfeld, Germany to pre-sulfide the catalyst via the methods developed in these pilot plant studies.

The XpresS Process

TRICAT's new XpresS process is shown schematically in Figure 4. The design, which can accommodate both fresh and regenerated catalyst, incorporates several features from the TRICAT regeneration process. Both the sulfiding and passivation reactors utilize an expanded bed, with the sulfiding gases (H_2 and H_2S carried in N_2) and passivation gases providing the means for bed expansion. The design is flexible to handle a range of catalyst sizes and shapes. Gas velocity is targeted to operate just above the minimum fluidization velocity for the catalyst in process. Bed expansion is typically in the range of 10-20%.

Each reactor is also baffled to ensure a tortuous path for the catalyst. As a result, the catalyst cannot short circuit through the reactors, ensuring that each particle is fully sulfided and subsequently passivated.

The sulfiding gases are recycled back through the reactor after particulate and water removal. An excess of H_2S is employed to ensure that catalyst reduction does not occur. Residual H_2S , including any stripped off in the passivation reactor, is scrubbed from the effluent gas.

The final step before packaging is screening to remove any fines generated during the process or contained in the feed.

The sulfided product is typically packaged in drums or flow bins. Although the XpresS pre-sulfided catalyst is stable in air even at temperatures up to $100^\circ C$, it is classified as a self-heating inorganic solid (UN-3190). This classification indicates that when heated in flowing air to $140^\circ C$ ($284^\circ F$), the material will heat spontaneously to a temperature above $200^\circ C$ ($392^\circ F$). XpresS pre-sulfided catalyst will self heat under

these extreme conditions. As a result, XpresS pre-sulfided catalyst must be packaged in conformance with the referenced standards.⁶ Catalyst pre-sulfurized, via technologies referenced earlier, also do not pass this "self-heating" standard, and are classified and packaged in the same fashion as XpresS catalyst.

The XpresS Start-up

Starting up a hydroprocessing unit after treating the catalyst via the XpresS process is greatly simplified. The speed of the start-up is mainly governed by the metallurgical limits of the unit. After the catalyst is loaded, and the unit is purged with nitrogen; hydrogen circulation is initiated without recycle gas scrubbing.

Pressure is increased in accordance with metallurgical limitations to about 400 psig. Reactor heat-up is then initiated at 50-75°F per hour. Once the reactor walls have reached 250-300°F, the reactor pressure can be raised to full operating pressure. Heat-up is resumed, and feed is introduced at the appropriate temperature for the feedstock.

In contrast to start-ups using in-situ sulfiding or pre-sulfurized catalyst, XpresS start-ups experience no exotherms, and no water is liberated.

Commercial Test of XpresS Pre-Sulfided Catalyst

The first commercial test of the XpresS technology was carried out in late 1997 at the OMV refinery in Burghausen, Germany. TRICAT regenerated and sulfided a small lot of a widely-used CoMo catalyst for use in a pyrolysis gasoline hydrodesulfurization unit. Based on the cobalt and molybdenum content of the regenerated catalyst, and the equations in Table 1, we expected 9.4 wt% sulfur to be deposited on the sulfided catalyst. The actual sulfur content was 8.3 wt%, or about 90% of the theoretical sulfur loading. The catalyst was reloaded into the unit and topped off with about 20% pre-sulfurized, regenerated catalyst from the refinery's inventory.

Figure 5 shows the temperature profile from the unit during start-up. Upon the introduction of hydrogen at ~150°F, a maximum exotherm of less than 10°F was observed in the top portion of the reactor throughout the heat-up. This is consistent with the literature for the pre-sulfurized product

employed in the top 20% of the reactor.² This exotherm dissipated along the length of the bed, indicating that the XpresS pre-sulfided catalyst was experiencing no exothermic sulfiding reactions.

The refinery typically introduces oil to this reactor at 460°F. However, to comply with the start-up guidelines for the pre-sulfurized catalyst that was loaded in the top of the bed; the refiner raised the temperature to 595°F briefly before reducing back to 460°F. As shown, this additional step (which would not have been necessary with the XpresS pre-sulfided catalyst), cost the refiner an additional 6-8 hours of start-up time.

OMV reported that the start-of-run activity was within the expected range for the unit. Aging also proved to be typical throughout the relatively short cycle typically experienced for this unit.

Conclusions

TRICAT's new XpresS pre-sulfiding process successfully activates hydroprocessing catalyst, and enables refiners to simplify and accelerate the hydroprocessing unit start-up procedure. The plant is able to process a broad range of hydroprocessing catalyst, including the variety of shapes and sizes currently employed.

Pilot-plant testing has confirmed that catalysts activated via the XpresS procedure are as active as those sulfided in-situ using the latest techniques.

The first commercially pre-sulfided catalysts produced via the XpresS process at TRICAT's new Bitterfeld, Germany plant have confirmed that the pre-sulfided catalyst is stable in air. The first commercial start-ups with the XpresS pre-sulfided catalyst have confirmed that the start-up can be achieved with no exotherm, and is greatly accelerated.

REFERENCES

1. Zeuthen, Per, et al., "Temperature-programmed sulfidation and oxidation of Ni-Mo/alumina catalysts and reaction with ammonia". Applied Catalysis, 68 (1991); pp 117-130.
2. Blashka, Stephen, et al. "New presulfurized catalyst reduced exotherm potential in hydrocrackers". Oil & Gas Journal, January 5, 1998; pp 36-40.
3. de Wind, Menno, et al. "Air quality and economics spur use of presulfided catalysts". Oil & Gas Journal, February 24, 1992; pp 49-53.
4. Welch, J. Gary, et al. "New presulfiding technique proves successful in commercial trials". Oil & Gas Journal, October 10, 1994; pp 56-64.
5. Neuman, Daniel J. "Novel Ebullated Bed Regeneration Technology Improves Regenerated Catalyst Quality". Presented at the 1995 NPRA Annual Meeting, San Francisco, March 1995.
6. Code of Federal Regulations, Volume 49, Sections 171-173.

Table 1

Sulfiding Reactions

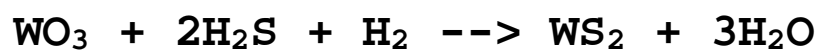
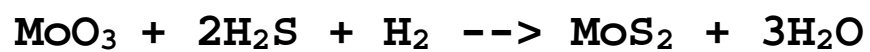
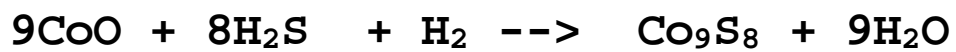


Table 2

NiMo Catalyst Sulfiding

Ni on catalyst	3 wt%
Mo on catalyst	14 wt%
Theoretical sulfur level on sulfided catalyst ¹	10.4 wt%

Pilot Plant Pre-sulfiding results
(dry basis)

Total Sulfur Content	9.6 wt%
Sulfur as S-	8.7 wt%
Sulfur as SO ₄ -	0.5 wt%
Sulfur as SO ₃ -	0.4 wt%

Note 1: Theoretical sulfur content calculated from sulfiding reaction equations in Table 1. Assumes all Ni and Mo sites are available for sulfiding.

Figure 1

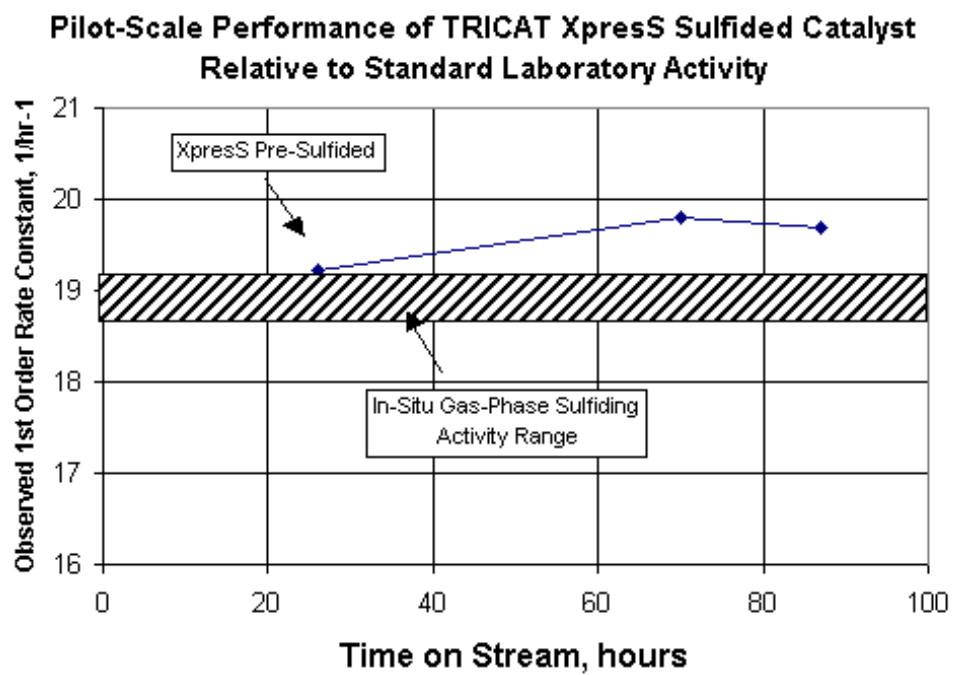


Figure 2

Activity of XpresS Pre-Sulfided Catalyst
Desulfurization Activity

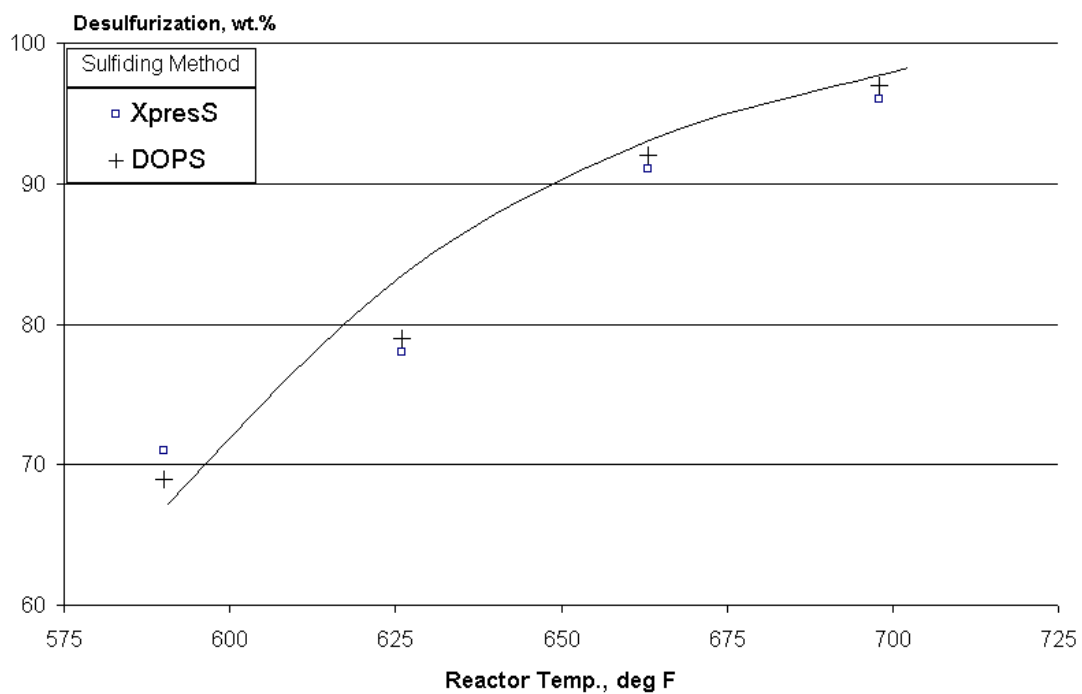


Figure 3

Activity of XpresS Pre-Sulfided Catalyst
Denitrogenation Activity

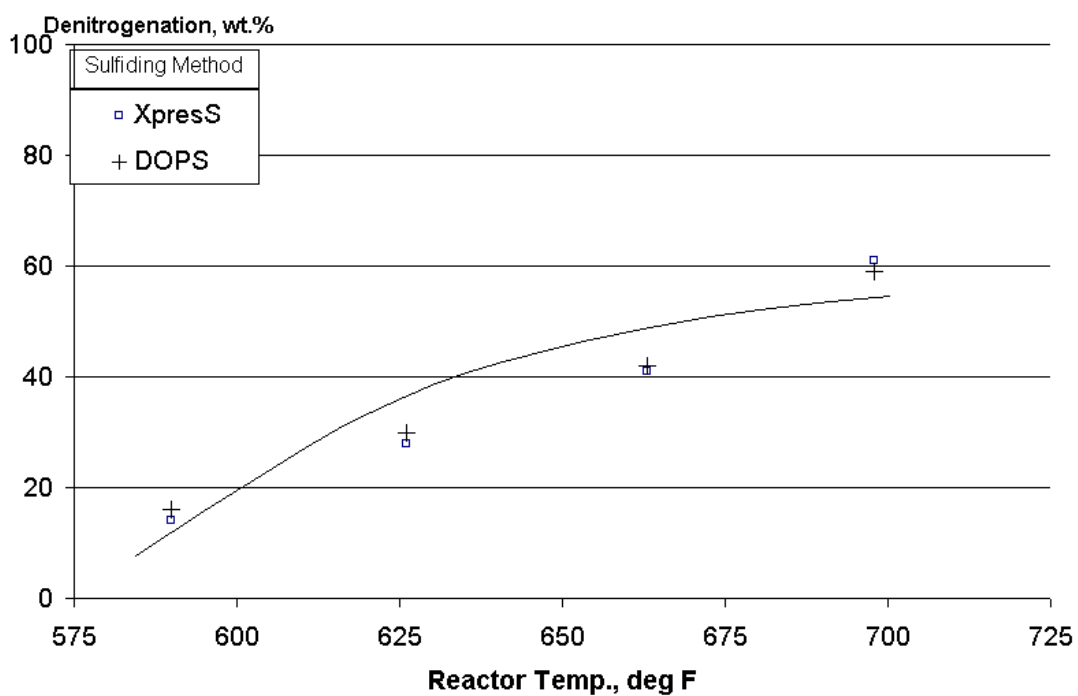


Figure 4

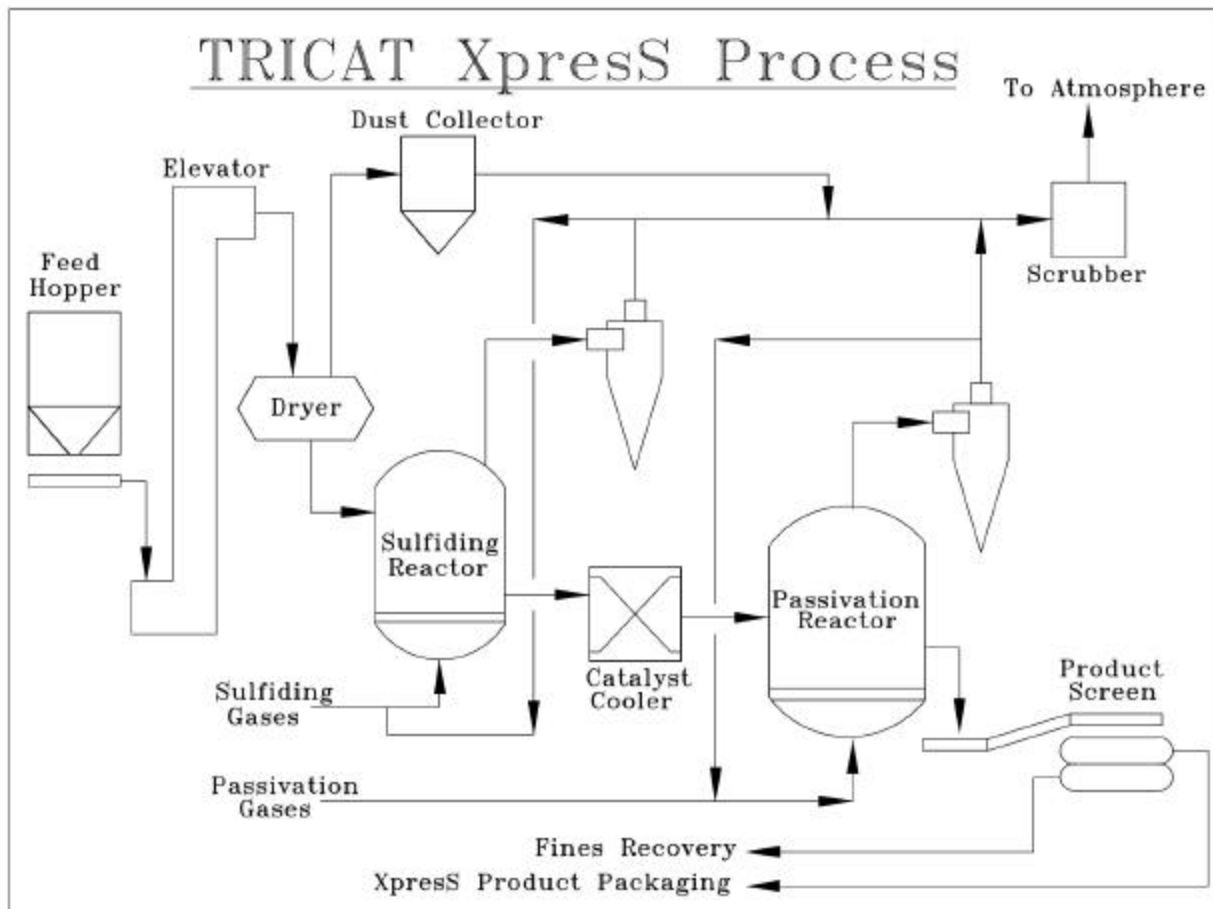


Figure 5

XpresS Start Up
Commercial Data - OMV Burghausen

