PROPER DESIGN AND OPERATION OF NHT CFE EQUIPMENT

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ABSTRACT

Many refineries in the US have been in operation for decades. Over this time, operating parameters may have shifted resulting in operation outside the original design of equipment. Reviewing current design criteria against current operation is a recommended action for all refiners. This paper will explain the current state-of-the-art criteria for process design and metallurgy selection.

PROCESS DESIGN PRACTICES

This section will review, from a process licensor's perspective, some key parameters and operational considerations that go into designing the combined feed exchanger for a low severity naphtha hydrotreating (NHT) unit.

The NHT unit prepares feedstock for downstream reforming or isomerization units that have sensitive noble metal catalyst systems. The schematic diagram in Figure 1 shows that naphtha feedstock is brought into the unit then mixed with hydrogen rich recycle gas. The combined feed is heated first by recovering heat from the reactor effluent in a combined feed exchanger (CFE), and then heated to reaction temperature in a fired charge heater.

The reactor contains a cobalt-molybdenum or nickel-molybdenum catalyst system that converts the contaminants of noble metal catalyst systems, such as sulfur, nitrogen, oxygenates, and halides via hydrogenolysis reactions to hydrogen sulfide, ammonia, water and hydrogen halides so they can be removed from the hydrocarbon stream. Metals in the naphtha are removed by adsorption onto the catalyst and low levels of olefins or trace diolefins are saturated. The hydrotreating reactions are exothermic with olefin saturation having the highest heat of reaction.

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Figure 1
Typical Flow Scheme of the Reactor Section of a Low Severity NHT
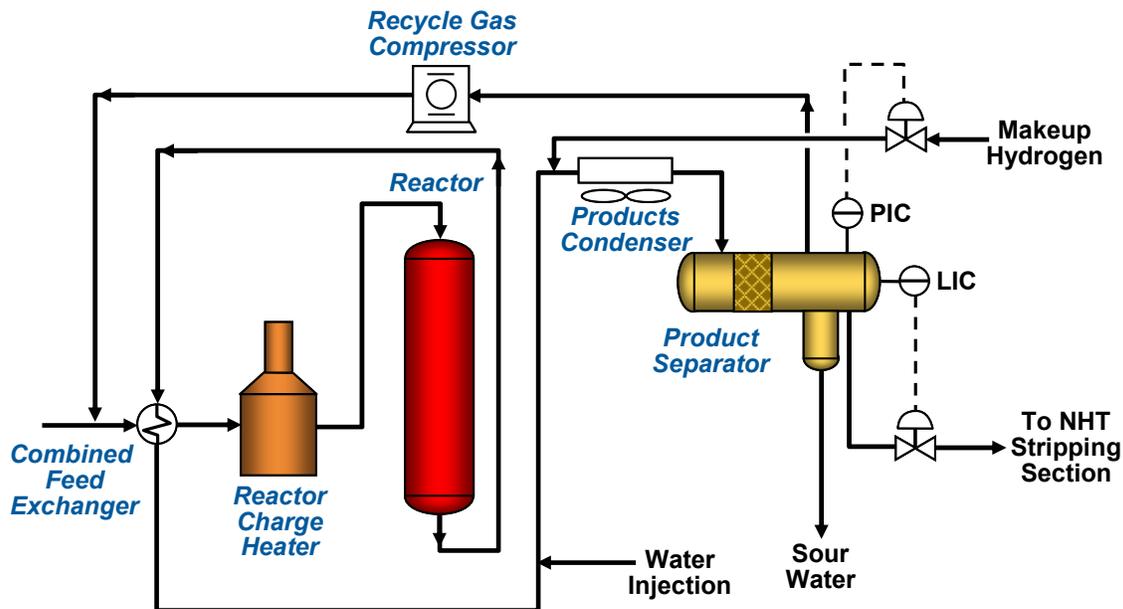
The reactor effluent is cooled in the CFE. Wash water is injected directly downstream of the CFE. The reactor effluent is further cooled in the products condenser and the three phases in the stream are separated in the product separator. Makeup hydrogen is introduced into the reactor circuit on pressure control.

The gas from the product separator is recycled back to the reactor. An equilibrium level of hydrogen sulfide builds up with the recycle gas scheme. The hydrotreated naphtha from the separator is sent to a stripping column to remove hydrogen sulfide, water and light ends before being fed to a downstream unit. Sour water containing ammonia, hydrogen chloride and equilibrium hydrogen sulfide is removed from the boot of the separator for further processing.

The naphtha feedstock to a low severity NHT unit would contain less than ~20% cracked stock. Moderate operating conditions are employed with pressure set in the range of 285-800 psig [20-55 kg/cm^2(g)]. Hydrogen circulation is set to achieve a target partial pressure to ensure the desired conversion of the defined contaminants and undesirable components. Temperature is increased in the range of 600-650°F [315-345°C] over the life of the catalyst. The temperature increase across the reactor bed is less than 50°F [28°C].

The discussion above shows that an important part of the NHT unit design is to understand the source of the naphtha feed and makeup hydrogen to be able to adequately quantify the expected contaminant levels, as well as trace elements that may not set the severity of the unit but will impact the design. Some particular considerations for CFE design will now be discussed.

Care must be taken in how the naphtha feed is brought into the unit. Sending naphtha with olefinic or diolefinic compounds through storage tanks, even if gas blanketed, would greatly increase fouling in the reactor circuit, including the combined feed exchanger. This operating scenario should be avoided. In units where the naphtha feed is transported to the refinery, oxygen contamination would most likely have occurred during transportation. To minimize fouling from oxygen contamination in that situation, an oxygen stripper should be considered to remove free oxygen and break down any peroxides formed.

Determining the chloride level in the naphtha and makeup gas is important to CFE design. Because the unit is not water free, corrosion could be an issue on both sides of the CFE. A second concern is that the hydrochloric acid and ammonia conversion products react to form corrosive and fouling ammonium chloride salts which precipitate out as the reactor effluent cools. As discussed above, water washing downstream of the CFE is used to solubilize these components. Because salt formation is a function of contaminant level and operating conditions, continuous wash water downstream of the CFE ensures that if the contaminant levels in the naphtha or makeup gas fluctuate, the equipment in the circuit is always protected. During CFE design, an additional analysis is performed to determine which exchanger salts could precipitate out based on the operating conditions. An intermittent wash water injection point is included upstream of the bundle where the salts are likely to form to allow flushing if thermal or hydraulic performance decreases. Since some liquid water is necessary to ensure proper flushing, the intermittent water washing point should not be set farther upstream than required. If detectable levels of chlorides are expected in the feed, the metallurgy selection of the unit is affected. If cost of exotic metallurgy is an issue, limiting the number of affected CFE shells could also be considered.

For NHT CFE service, horizontal shell and tube exchangers tend to be specified since they are cost effective and easily cleanable. Hydrotreating reactions are not pressure sensitive enough to benefit from the low pressure drop, high heat recovery but higher cost of vertical or welded plate style exchangers. Also, vertical and welded plate exchangers can be difficult to clean if gums or salts must be removed.

The choice of whether to place the feed on the shell or tube side of a bundle is not always straightforward. Economic considerations show higher pressure feed is placed on the shell side and higher temperature reactor effluent is placed on the tube side. Although it is usually more economical to put the process fluid with the highest temperature on the tube side, another consideration for the CFE is the ability to flush out ammonium chloride salts.

Since the combined feed exchanger utilizes heat in a process stream that requires cooling, pinch analysis helps determine the optimum heat exchanger network. Practical operating procedures

also need to be considered. For example, if the naphtha feed contains some olefins, a significant temperature increase results across the reactor. Pinch analysis shows only a small charge heater is required. Startup considerations, as well as potential alternate operation with a straight-run only feed leads to consideration of a larger charge heater. The analysis must also achieve an all-vapor stream to the charge heater.

Once the process boundaries are defined, an analysis is done to compare the economics of incremental exchanger surface area offset by reduced fuel firing and air cooling costs to arrive at the right approach temperature, taking into account the corrected log mean temperature difference (LMTD). Most mixed-phase shell and tube heat exchangers have overall heat transfer coefficients (OHTCs) between 50 and 70 and this number is used for preliminary sizing of exchangers for the various cases. The allowable pressure drop per shell is 5 psi (0.35 kg/cm^2) shell side and 5 psi (0.35 kg/cm^2) tube side. Typical TEMA fouling factors are assumed to ensure adequate shell and tube velocities. If higher fouling factors are assumed than required, the resulting low velocities could cause increased fouling. Economic analysis shows that generally 4 to 8 shells in series can be expected.

The overall results are summarized in an exchanger project specification. To set the CFE design pressure, the reactor circuit hydraulics are analyzed, including any expected long term operations. For example, over the life of the catalyst, the top of the reactor can collect scale and gum which plug the top of the bed. A plugging allowance for this scenario is included when setting the design pressures of the equipment in the circuit. Design to the 10/13th rule is not applicable for this service due to the presence of two-phase flow. A pressure surge due to a tube leak/rupture from the high pressure side to the low pressure side is minimized by the compression of the vapor on the low pressure side. However, the 10/13th criteria is often exceeded as the ratio of operating and design pressures is greater than 10/13 as they differ by a relatively small pressure drop in the circuit compared to actual pressure. Design pressure of the CFE is not graded. During startup, the reactor circuit is evacuated with an ejector to air-free the system. The exchanger is designed for full vacuum at the expected startup design temperature.

The CFE design temperatures are graded for cost effectiveness. All expected operating scenarios must be considered. Alloy selection for each shell is selected based on expected operating temperatures. If the number of shells is altered during the detailed design phase, it is essential that the metallurgy selection be reviewed with the change.

The exchanger project specification for this service shows TEMA type BEU exchangers are typically selected for this service. The U-type tube bundle is cost effective and minimizes the joints where leakage may occur. UOP specifies them when the exchanger is in hydrogen service, defined as having a hydrogen partial pressure of 50 psia [3.5 kg/cm^2(a)] or greater, or for a service containing 90 vol% or higher at any pressure level.

Horizontal baffle cuts are not used for the NHT CFE because the feed is two phase. A vertical cut is used to ensure more even distribution of both phases around each baffle and reduce the potential for slug flow. All exchangers in process service are designed to the ASME Section VIII Code and to the requirements TEMA. Application of the TEMA Class R, Refinery Standards is required. UOP requires the use of at least a ¾ inch OD tube.

The exchanger project specification may specify strength-welded tube to tubesheet joints to prevent or minimize the possibility of cross leakage. For a typical NHT operation, strength-welding is not required because the unit can operate if minor cross-leakage occurs. Strength-welding is required if a sulfur-sensitive isomerization unit is downstream of the NHT unit. When strength welding is required, the metallurgist needs to know upfront to ensure that the metallurgy selected allows for welding.

For a typical size unit, the CFE consists of one parallel train of multiple horizontal shell and tube heat exchangers in series. Since the reactor circuit is designed to be open without valving, PRV protection for exchangers alone is not required. With large units, the shell diameter may be limited by bundle pulling capacity necessary to clean and maintain the exchangers. If parallel shells are required, care should be taken to ensure equal flow distribution between trains. If a known fouling service exists and parallel trains are desired to allow cleaning without shutting the unit down completely, separate PRVs would need to be provided. Placement and relief destination of the hot streams would need to be considered.

Over the years, NHT operating temperatures have decreased due to concerns with formation of recombination sulfur products. Some feeds and reactor circuit conditions resulted in trace olefins and hydrogen sulfide recombining after leaving the reactor. To prevent this phenomenon, reactor temperatures were lowered to those specified today. Neutralization requirements for austenitic steel is therefore not itemized in the exchanger project specification for modern units and does not affect metallurgy selection.

Shell and tube heat exchanger temperature measuring equipment used to determine the performance of individual shells is not specified in the exchanger design specification. Typically, each refiner has specific requirements which are included on the piping and instrument diagram (P&ID) legend for implementation by the contractor. For the exchanger arrangement selected, the need to determine exchanger over- or underperforming should be considered on the process and equipment, as well as monitoring turndown, start-up and shutdown conditions.

METALLURGY SELECTION

Metallurgy selection for all UOP units begins with the generation of a Material Selection Diagram (MSD). An MSD shows all pieces of equipment in individual boxes. All major piping circuits are also shown; however, the MSD does not contain the level of detail of a P&ID. The MSD will give design temperatures and pressures, maximum operating temperatures, hydrogen partial pressures, and concentrations of contaminants such as sulfur, H_2S, ammonia, chlorides, etc. MSDs are generated in accordance with the guidelines of NACE SP0407 (1).

Specific to hydroprocessing units, UOP adds to the MSD a Metallurgy Review Information Sheet (Figure 2). The Design Engineer fills in the process details for the shell side and tube side for each exchanger in the train, along with maximum operating temperatures for the interconnecting piping (if any).

Figure 2
Example of a Metallurgy Review Information Sheet

The metallurgy selection process for the CFEs begins with a check of temperature and hydrogen partial pressure against the curves in API 941 (2), sometimes referred to as the "Nelson Curves" after their originator. This check is done for both the shell side and tube side conditions. UOP uses design temperature and design pressure for this check, not operating temperature and pressure. This adds two layers of conservatism to our design. The required metallurgy for each side will be recorded, and this sets the minimum required metallurgy. However, the metallurgy will frequently need to be upgraded due to corrosion considerations as will be discussed later.

The next step in the metallurgy selection process is to determine corrosion rates. The corrosion rate on the effluent side will always be governed by H_2/H_2S corrosion. The corrosion rate on the feed side of the exchanger must consider high temperature sulfidic corrosion. However, the recycle gas, which contains H_2S, is sent back to the reactor through the CFE. In addition to high temperature sulfidic corrosion, the feed side may also see H_2/H_2S corrosion, and whichever is higher will govern. To make these determinations UOP uses proprietary corrosion rate curves. Our corrosion rate curves are experience-based adaptations of curves available in the public domain (3) (4). Note that for the tubes, corrosion occurs from both sides. Therefore, the corrosion rates are added to determine a total corrosion rate for the tubes.

UOP designs the CFEs to a 20 year design life. In order to meet this design life, UOP will add corrosion allowance or upgrade metallurgy as necessary. UOP will add corrosion allowance only up to ¼ in. (6 mm). As mentioned previously, this frequently results in upgrading metallurgy from what was indicated by the API 941 curves. If a ¼ in. (6 mm) corrosion allowance will not result in meeting or exceeding the design life for the shell, channel, and floating head, a stainless steel lining will be specified.

For the tubesheet, if the corrosion rate on the tube side is high such that the tubesheet will not meet the design life criteria, we will specify lining on the tube side with stainless steel. We also specify tube side lining with stainless steel if the tubes are stainless steel and they are to be welded to the tubesheet. If the corrosion rate on the shell side is too high, we will specify a solid stainless steel tubesheet.

Since corrosion allowance is not added to heat exchanger tubes, UOP limits the total corrosion rate (adding the corrosion rates from both sides) to 5 mils per year (0.127 mm/yr). This frequently results in upgrading the tube bundles to stainless steel.

Another consideration is the potential for ammonium chloride deposition. Ammonium chloride can be present in units that have higher than desired chloride levels in the feed or in the make-up hydrogen. For this reason, UOP prefers a feed chloride level not to exceed 0.5 ppm, and a maximum chloride level in the make-up hydrogen of 1 ppm. If the make-up hydrogen is coming

from a UOP Platforming™ Unit, we desire that the hydrogen go through a double chloride treater before coming into the NHT.

Ammonium chloride has a higher sublimation temperature than ammonium bisulfide (which precipitates in the air cooler), so the ammonium chloride, if present, will precipitate somewhere in the CFE train. If this is a possibility, the Design Engineer will indicate to the metallurgist on the MSD in which exchanger the precipitation will occur. Wash water injection nozzles will be specified for this exchanger to prevent fouling of the exchanger in service. Because wet ammonium chloride is extremely corrosive, the metallurgist will upgrade the tubes and lining in this exchanger to Alloy 625.

A final consideration in the metallurgy selection for CFEs is wet H_2S at the cold end of the exchanger train. UOP has adopted the definitions of wet H_2S service given in NACE Standard MR0103 (5). The concern with wet H_2S is that it can not only cause general corrosion, it can also cause sulfide stress cracking (5), as well as blistering, hydrogen-induced cracking, and stress-oriented hydrogen-induced cracking (6). To mitigate these concerns, when a piece of equipment made of killed carbon steel is designated as wet H_2S service, UOP will add a 3/16 in. (5 mm) corrosion allowance (1/8 in. -- 3 mm for piping), and specify postweld heat treatment. If the H_2S concentration is equal to or greater than 25%, we will line the vessel with Type 316L stainless steel and upgrade all associated piping to solid Type 316L.

REFERENCES

(1) Standard Practice SP0407, "Format, Content, and Guidelines for Developing a Materials Selection Diagram," Item No. 21123, 2007, NACE International, Houston, TX

(2) API Recommended Practice 941, "Steels for Hydrogen Service at Elevated Temperature and Pressures in Petroleum Refineries and Petrochemical Plants," 2008, American Petroleum Institute, Washington D.C.

(3) A. S. Couper and J. W. Gorman, "Computer Correlations to Estimate High Temperature H_2S Corrosion in Refinery Streams," *Materials Protection and Performance*, Vol. 10, No. 4, p. 17-22, 1971

(4) H. F. McConomy, "High Temperature Sulfidic Corrosion in Hydrogen-Free Environments," API Proceedings, Vol. 43, (III), p. 78-96, 1963

(5) Standard Material Requirements MR0103, "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments," Item No. 21305, 2007, NACE International, Houston, TX

(6) Standard Practice SP0296, "Detection, Repair, and Mitigation of Cracking in Refinery Equipment in Wet H_2S Environments," Item No. 21078, 2010, NACE International, Houston, TX