SIMULTANEOUS EFFECTIVE REMOVAL OF POLYSULFIDE AND POLYOLEFIN FOULING FROM TWISTED TUBE®® HEAT EXCANGERS IN HYDROCRACKER PROCESS USING ULTRASONIC CHEMICAL CLEANING

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ABSTRACT

This paper investigates the intricate facets of cleaning complex heat exchanger units from the Hydrocracker process unit in a refinery which utilizes opportunity crude feedstock. The exchangers in question are of 300-series stainless steel TWISTED TUBE® design. The fouling present on the exchangers proved to be polymeric olefin fouling on the shell side and a combination of iron sulfide (FeS_2) and Metal Polysulfide (Me_xS_y) on the tube side.

Due to the high pressure and high temperature of the hydrocracker process, considerations regarding the potential for polythionic stress corrosion cracking needed to be considered, which imposed strict conditions on the chemical cleaning agent to be used and posed an ideal opportunity for ultrasonic immersion technology to be highlighted. A safe and effective ultrasonic cleaning protocol was employed which removed the fouling on both the tube side and the shell side of the exchangers simultaneously.

INTRODUCTION

The hydrogen cracking unit, or hydrocracker, in a refinery takes low-quality heavy gas oils from various units and converts them through a series of catalytic reactions into high-quality, clean burning fuels, such as gasoline, diesel and jet fuel. The process feed for the hydrocracker comes from the atmospheric and vacuum distillation towers, the fluid catalytic cracking (FCC) unit, and the coker units. The feed is typically contaminated with high sulfur and nitrogen and may also be heavy in metallic compounds.

The hydrocracking process typically uses Platinum/Zeolite catalysts to take the high-boiling, high-molecular weight hydrocarbons and 'crack' them into smaller lower-boiling point and lower-molecular weight olefinic and aromatic hydrocarbons, which are then hydrogenated through the addition of hydrogen gas to the system. During this process, the bulk of the sulfur or nitrogen contaminants are also hydrogenated and form the gaseous by-products hydrogen sulfide (H_2S) and ammonia (NH_3) which are either vented to flare, or removed through amine scrubbing. Metal contaminants are also removed during the hydrocracking processes, though careful selection of the catalysts must be considered to obtain reasonable catalyst life. Figure 18, located in the Appendix, shows a process diagram for the Hydrocracker unit.

This paper describes our work in cleaning the fouling from four 300-series stainless TWISTED TUBE® U-bend heat exchanger bundles from the hydrocracking process using ultrasonic chemical cleaning through the combination of ultrasonic immersion technology and proprietary chemical blends tailored to the process foulant. The mechanism of action for the ultrasonic cleaning technology is further described in Kieser at al. (2011) [1]. The first bank of heat exchangers E-1 and E-2 are in series in the Second Stage of the process; where, the shell side process is the feed to the Second Stage Reactor and the tube side process is the effluent from the same reactor. The second bank of heat exchangers E-3 and E-4 are also in series but are in the first stage of the process; where, the shell side process in the feed to the First Stage Reactor and the tube side process is the effluent from the same reactor. The location of these exchangers in the process can be seen in figure 18, in the appendix.

Heat Exchanger Design

TWISTED TUBE® heat exchangers are designed for highly efficient heat transfer and reduced fouling. The U-bend design allows for accommodation of thermal expansion and provides a greater heat transfer surface area. The heat exchangers in the hydrocracker unit operate under high temperatures and high pressures for which thermal expansion and heat transfer is extremely important. Furthermore, for the heavy, sour crudes the hydrocracker feed can be a high fouling process stream susceptible to corrosive attack. Therefore, TWISTED TUBE® heat exchangers were chosen to meet the requirements of the process, and has extended the runtime for this process unit greatly due to the lower fouling rate.

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Once fouled, however, these exchangers can be difficult to clean due to the compact design. The tubes are set in a 30°/60° triangular pitch offering a close-packed geometry. In this style of heat exchanger the tubes are self-supporting, and these may shift over time allowing cleaning lanes to become less accessible in older bundles, particularly around the U-bends. As a result the central core of the bundle, denoted in figure 1 by the red polygon, is a challenge to clean on the shell side. Furthermore, the oblong TWISTED TUBE® design which creates the turbulent flow in the tube side process makes the tubes difficult to clean. Figure 2 shows the tube internal geometry as it changes with the twists in each tube.

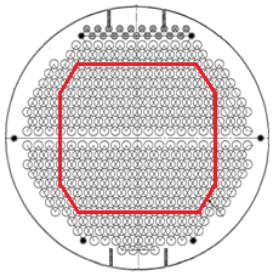

Fig. 1. Tubeface for TWISTED TUBE® heat exchanger showing the triangular (30°/60°) arrangement. The area in red denotes the core of the bundle which is difficult to clean on the shell side.

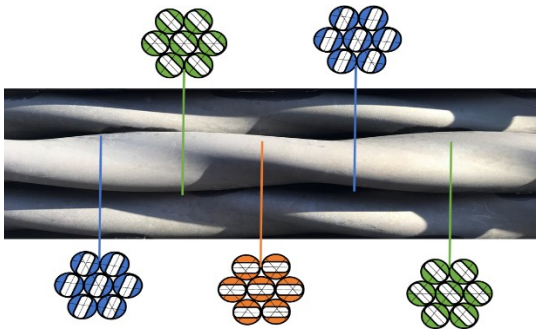

Fig. 2. Depiction of the narrow turbulent path inside TWISTED TUBE® heat exchanger bundles on the tube side.

Previous Cleaning Attempts

Previous attempts to chemically clean the bundle in-place were unsuccessful. On the shell side this was due to the polymeric scaling which creates a uniform, thin layer on the tube surface. Traditional chemical cleaning would need to dissolve this type of foulant from the tube surface. Ultrasonic Chemical Cleaning, however, uses tailored chemistries which saturate and penetrate the foulant layer, combined with ultrasonic cavitation which fractures the brittle scale and dislodges it from the equipment surface.

On the tube side, the polysulfide foulant requires specialty chemicals which fall on the acidic range on the pH spectrum. Due to concerns from the unit engineering team regarding the potential for polythionic stress corrosion cracking due to the high temperatures and pressures observed in these exchangers, acidic chemistries for the clean-in-place techniques were to be avoided.

Furthermore, during a previous outage, these bundles were cleaned through a combination of chemical cleaning, delivered in place, and then removed from service for high pressure water blasting (HPWB) at a maximum pressure of 40,000 psi. The bundles were returned to service in a partially fouled condition after 14 days of hydroblast activity as the Lost Profit Opportunity (LPO) of having these exchangers out of services any longer drove the decision to put the exchangers back in service. The total downtime for the unit was 21 days, including the time to chemically clean, pull the bundles and put them back into service. Fig. 3 and Fig. 4 show that this previous attempt at cleaning was unsuccessful from a visual standpoint. The client also stated that very little improvement to the heat transfer coefficient was gained from this cleaning.

Fig. 3. Previous Cleaning Attempt. Tube Side fouling layer still observed after chemical cleaning in-place and HPWB.

Fig. 4. Previous Cleaning Attempt. Shell Side fouling layer still observed after chemical cleaning in-place and HPWB. Debris still built up between the tubes as evidenced by the Dip Stick verification.

METHODS

To best understand the foulant and provide a confident chemical recommendation, samples from the previous cleaning were assessed by Powder X-Ray Diffraction (PXRD) and Energy-Dispersive X-Ray Fluorescence (ED-XRF), in combination with

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quantitative chemical analysis. The main constituents of the foulants on the tube side and the shell side are given together in table 1.

The main foulant on the shell side of the bundles, shown in Figure 5, proved to be polymeric olefin (polyolefin) compounds, and was mixed with calcium silicate, in the form of diopside ($CaMgSi_2O_6$) and $CaSiO_3$, Crystalline coke particulate in the form of Graphitic Carbon (C), and iron phosphate (Fe_3PO_4) or Magnetite (Fe_3O_4). The shell side fouling has been the primary area of concern in the cleaning of these bundles.

Fig. 5. Sample Image of the Shell Side Foulant on the TWISTED TUBE® Heat Exchangers Studied Before Cleaning.

Table 1. Chemical Characterization of TWISTED TUBE® Heat Exchanger Bundle Samples

	Component	%wt
E-1 Shell	Polyolefin scale (hard scale)	61.2
	Iron Phosphate (Fe_3PO_4)	20.2
	Light Hydrocarbon	11.1
	Graphite (C)	7.5
E-1 Tube	Chromium Sulfide (Cr_7S_8)	48.1
	Troilite (FeS)	37.6
	Light Hydrocarbon	14.3
E-2 Shell	Polyolefin Scale (hard scale)	49.1
	Iron Phosphate (Fe_3PO_4)	31.2
	Light Hydrocarbon	10.3
	Graphite (C)	9.4
E-2 Tube	Chromium Sulfide (Cr_7S_8)	85.4
	Light Hydrocarbon	14.6
E-3 Shell	Diopside ($CaMgSi_2O_6$)	43.8
	Polyolefin/Hydrocarbon (sticky, soft)	40.6
	Iron Phosphate (Fe_3PO_4)	15.6
E-3 Tube	Chromium Sulfide (Cr_7S_8)	38.1
	Troilite (FeS)	24.0
	Pentlandite [$(Fe,Ni)_9S_8$]	14.6
	Light Hydrocarbon	23.3
E-4 Shell	Polyolefin/Hydrocarbon (sticky, soft)	36.9
	Calcium Silicate ($CaSiO_3$)	30.4
	Graphite (C)	28.8
	Magnetite (Fe_3O_4)	3.9
E-4 Tube	Chromium Sulfide (Cr_7S_8)	45.7
	Troilite (FeS)	23.1
	Pentlandite [$(Fe,Ni)_9S_8$]	17.3
	Light Hydrocarbon	13.9

The bundles from the Second Stage Reactor (E-1 and E-2) exhibited a polyolefin fouling that was hard scale (observed in figure 6), that required some scraping to remove from the tube surface. This is to be expected given that the process fluid for these bundles was the reactor feedstock for the Second Stage Reactor. This process fluid is the effluent from the fractionator which recycles the effluent from both the first stage and second stage reactors. Thus, it is to be expected that this will contain primarily partially reacted olefins, catalyst fines and coke.

The bundles from the First Stage Reactor (E-3 and E-4) exhibited a polyolefin foulant that was soft, greasy and sticky, and had a gum-like consistency. Rubbing resulting in a smearing effect (observed in figure 7). The feedstock for E-3 and E-4 is the hydrocracker feed which will be a combination of all the recycled gas oils from the atmospheric and vacuum distillation towers, the FCC and the coker units. Thus, the feed is expected to contain heavy gas oils, partially reacted olefins from the FCC, and coke.

Fig. 6. Exchanger E-2 Shell Side Foulant

Fig. 7 Exchanger E-4 Shell Side Foulant

The primary foulant on the tube side was a combination of iron sulfides (FeS) and pyrophoric metal polysulfides (Me_xS_y) such as Chromium Sulfide (Cr_7S_8) and Pentlandite [$(Fe,Ni)_9S_8$]. Although, a stabilized hydrogen peroxide would have been the preferred cleaning agent for the tube side fouling, the low pH (3.0-3.5) for the chemical blend raised some concerns for the unit engineers. Although unlikely to occur under ultrasonic conditions, the possibility that the acidic solution may result in the metallurgy of the material to become susceptible to polythionic stress corrosion cracking under the high temperatures and pressures exerted on the equipment during the hydrocracking process was taken under consideration and resulted in the need to go to more alkaline conditions. Ultrasonic chemistry was formulated and selected based on criteria laid out in Shank et. al. (2021) [2]. The criteria for the chemistry includes, but is not limited to:

- Effectiveness of the chemistry on the deposit
- Compatibility with the metallurgy
- Chemical Loading/Spending
- Corrosion Control
- On-site Testing Criteria

Both the polysulfide and polyolefin foulants are particularly adherent to iron-based metallurgies, and HPWB is rarely effective in either case. Both polysulfide and polyolefin are insulating compounds and affect the heat transfer for these bundles.

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The ultrasonic immersion technology was chosen for this cleaning application as it allows for the cleaning of all the interstitial spaces in the heat exchanger bundle simultaneously using both chemical and mechanical cleaning. The cavitation effect of the ultrasonics on the cleaning fluid results in a fact and effective dislodging of hard scales. This ultrasonic technique was combined with a degreasing surfactant blend with a pH of 12.5 and the addition of an asphaltene dispersant to treat both the tube side and shell side foulants simultaneously.

After 8-10 hours of ultrasonic action, depending on the severity of the shell side fouling, the item was removed from the ultrasonic vessel and a shell side bundle blaster was used to knock off any residual shell side fouling using only 20,000 psi water pressure. The tubes were flushed with low-chloride water using a fire hose nozzle. Total hydro blast time per bundle was between 4-6 hours.

The channel heads on these heat exchanger bundles were fixed, which posed an additional challenge due to the considerations required for nozzle placement in the Ultrasonic bath. Figure 8 shows E-4 and the nozzle placement at 90°, 180° and 270° before it was placed in the Ultrasonic vessel and the accommodation for the channel head that was required to offer a 360° cleaning of the exchanger. Figure 9, shows this exchanger in the ultrasonic vessel in the initial orientation with one of the nozzles lowered into the vessel, and the final orientation.

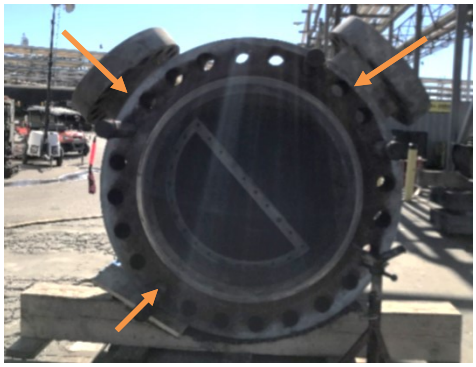

Fig. 8. E-4 Fixed Channel head view showing the layout of the three nozzles on the head at 90°, 180°, and 270°, denoted by the orange arrows.

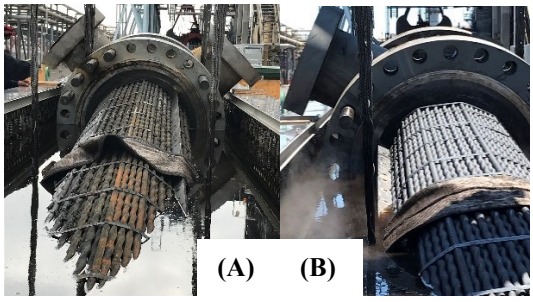

Fig. 9. E-4 accommodation in the Ultrasonic Vessel during (A) the initial immersion into the vessel and (B) the final immersion into the vessel.

The vessel used for this project was 8.5 m (28 ft) in length, 1.7 m (67 in) in width and 1.5 m (59 in) in depth. It should be noted here that larger vessels do exist and would have been able to completely submerge the exchanger with the channel heads and valves but were unavailable at the time of this project.

RESULTS

Four TWISTED TUBE® U-bend heat exchangers with fixed channel heads were cleaned. The exchanger E-3 was cleaned over 8 hours of ultrasonic immersion and 4 hours of HPWB on the shell side with low pressure flushing of the tube side. One of the exchangers (E-4) had to be accommodated for awkward orientations of the fixed channel head valves and required a second ultrasonic immersion to achieve 360° cleaning of the bundle. Therefore, this bundle took an additional 8 hours in the ultrasonic vessel. The shell side foulant on the other two bundles (E-1 and E-2) took an additional 2 hours to remove as the higher temperatures for the process of these two bundles resulted in a greater degree of polymerization of the polyolefin by-product.

Previous attempts at chemical cleaning these bundles were unsuccessful, and an attempt to HPWB these units during the previous outage saw the use of 40,000 psi water pressure for 14 days with little foulant removal, resulting in the exchangers being returned to service in a partially fouled condition, aggravating the fouling issue over the lifetime of the run.

Using ultrasonic cleaning, all four heat exchanger bundles were returned to the client in four days. Not only were these returned to the client 10 days faster than traditional methods, but these were also returned to service in like-new conditions, allowing for better heat transfer efficiency and volume throughput, and allowing for lowered greenhouse gas emissions through the reduction in overall fuel gas consumption. The ultrasonic immersion time was approximately 8-10 hours, and hydro blasting only requiring 4-6 hours post ultrasonic clean. This proved to be a large deviation in overall cleaning time required per bundle.

Before and after ultrasonic cleaning images are shown in figures 10 through 15 for the shell side and U-bend cleaning. Tube side cleaning was difficult to assess visually due to the fixed channel heads, but figures 16 and 17 attempt to draw the comparison, and borescope video indicated that the tube side cleaning had been successful.

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Fig. 10. E-1 Before - Shell Side Close up


Fig. 11. E-1 After - Shell Side Close up


Fig. 12. E-1 Before - U-bend Close up

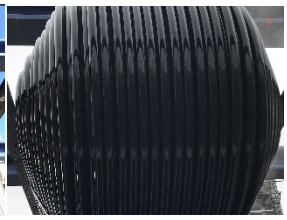
Fig. 13. E-1 After - U-bend Close up


Fig. 14. E-3 Before - Shell Side Banding


Fig. 15. E-3 After - Shell Side Banding


Fig. 16. E-4 Before - Tube Side Fouling

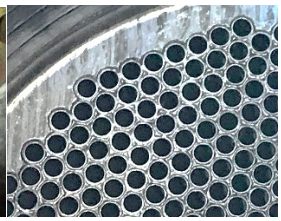
Fig. 17. E-4 After – Tube Side Cleaning

CONCLUSION

Ultrasonic immersion technology combined with selected chemistries is a fast and effective method for the simultaneous cleaning of parts and equipment. For equipment where the design makes it more difficult to clean than traditional styles, such as U-bend, Fixed Channel Heads, TWISTED TUBE® heat exchangers or welded plate exchangers (as seen in Philion et al. [3]), ultrasonic immersion offers a step change in service as cleaning lane constraints are sidestepped.

In many cases, where different fouling profiles are encountered on the tube side and shell side of an exchanger, chemical selection can become a challenge. In the case of this project, metal polysulfide and polyolefin foulant was encountered, each posing a significant challenge to traditional cleaning methods. Acidic chemistries could not be considered due to concerns regarding polythionic stress corrosion cracking of the bundle when returned to service. An alkaline degreasing chemistry was selected which proved to be effective in the removal of both the tube side and shell side foulants.

NOMENCLATURE

FeS_2 Iron Sulfide
Me_xS_y Metal Polysulfide
Cr_7S_9 Chromium Sulfide
$[(Fe,Ni)_8S_9]$ Pentlandite
Fe_3PO_4 Iron Phosphate
$CaSiO_3$ Calcium Silicate
$CaMgSi_6O_3$ Diopside
C Graphite
FCC Fluid Catalytic Cracking
H_2S Hydrogen Sulfide
NH_3 Ammonia
HPWB High Pressure Water Blasting
IPA Isopropyl Alcohol
HCl Hydrochloric Acid
HNO_3 Nitric Acid
ABF Ammonium Bifluoride
MP-AES Microwave Plasma Atomic Emission Spectroscopy
PXRD Powder X-Ray Diffraction
ED-XRF Energy Dispersive X-Ray Fluorescence
ATR-FTIR Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

REFERENCES

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APPENDIX

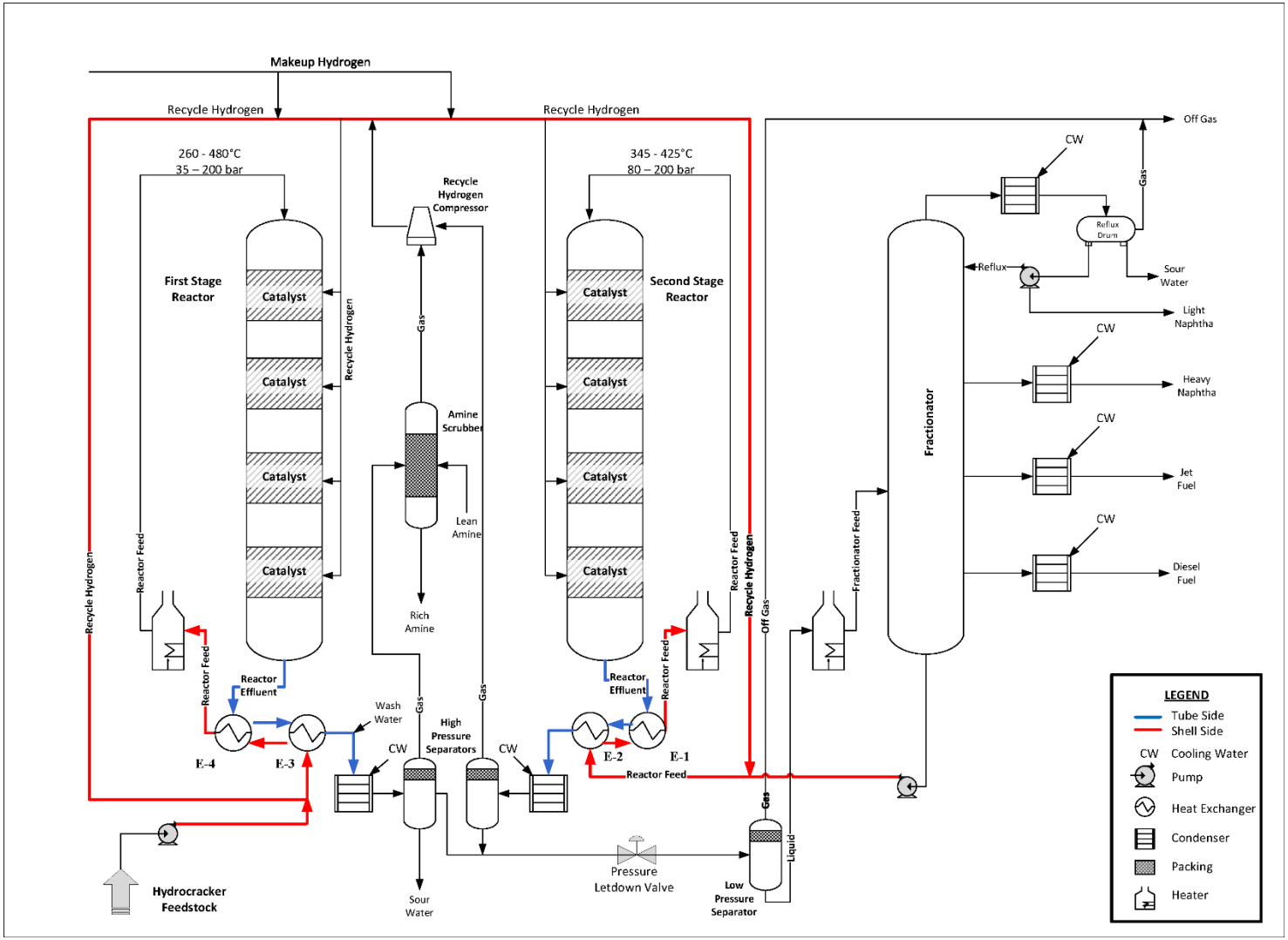

Fig. 18. Hydrocracker Process. Heat exchangers E-1 & E-2 are located below the Second Stage Reactor. Heat exchangers E-3 & E-4 are located below the First Stage Reactor. The tube side process fluid is the reactor effluent (blue); whereas, the shell side process fluid is the reactor feed (red).

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