Liquid Metal Corrosion Fluid Catalytic Cracking Units

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Abstract -- **Oil refineries use fluid catalytic cracking to correct the imbalance between the market demand for gasoline and the excess of heavy, high boiling range products resulting from the distillation of crude oil. Once upon a time, there was a fire in Fluidised Craking Unit in Baroda at Gujarat Refinery in the year, 1985. Orifice chamber of the unit is made up of SS 304. Over that insulation of glass bed and aluminum sheets were covered and were fixed up. During fire, the aluminum sheets were molten and impregnated into the SS 304 Orifice chamber walls. From outside the Orifice Chamber when it was repaired, there were so many holes like beehive due to molten aluminum. This phenomenon is known as liquid metal-to-metal corrosion. Remedial action taken: the covering of SS 304 was removed immediately.**

Keywords: Metal-to-metal corrosion, Fractionators, Catalytic cracking, Stress corrosion cracking, Liquid metal corrosion

I. INTRODUCTION

FLUID catalytic cracking (FCC) is the conversion process used in petroleum refineries to convert the high-boiling point, high-molecular weight hydrocarbon fractions of petroleum (crude oils) into gasoline, alkene gases, and other petroleum products. The cracking of petroleum hydrocarbons was originally done by thermal cracking, now virtually replaced by catalytic cracking, which yields greater volumes of high octane rating gasoline; and produces by-product gases, with more carbon-carbon double bonds (*i.e.* alkenes), that are of greater economic value than the gases produced by thermal cracking.

FCC involves cracking heavy oils or residuum feed-stocks by using elevated temperature, relatively low pressure, and a catalyst. Feedstocks for an FCC unit usually include straight run heavy gas oils and coke gas oils but, with more advanced catalysts, can include atmospheric residuum and vacuum tower bottoms. The boiling point for feedstock is generally in the 343°C to 593°C range. Temperature in the cracker vessel is usually 480°C.

Operating conditions, catalyst, and hardware are designed to maximize production of high-octane gasoline. During the cracking, reaction larger molecules are broken up and small amount of the carbon becomes coke, which is basically pure carbon atoms stuck together. When the larger molecules crack, those that consist of small rings (mostly aromatics and naphthenic compounds and some olefins) are produced. The products of catalytic cracking, therefore, include the full range of hydrocarbons from methane down to residuum and coke.

In fluidization, gas in the form of air, steam, or vaporized hydrocarbon is heated and travels through the powdered catalyst at a velocity sufficient to suspend it. This results in an aerated solid-gas mixture that acts as a boiling, bubbling fluid that is continuously circulated between the regenerator and reactor. This mixture enters the reactor through a line called a riser, which leads into the bottom of the reaction chamber. A considerable amount of the cracking process happens in the riser, so the actual time spent in the reactor is only a few seconds. The reactor is principally used as a catalyst/hydrocarbon separator.

Catalyst transport is controlled primarily by differential gas pressure between the regenerator and reactor, differential catalyst-gas mixture densities, and slide valves that act as control valves.

II. HARDWARE

FCC units comprise four principal component systems:

- Riser/reactor
- Regenerator
- Flue gas system
- Main fractionator.

Riser/Reactor: The riser/reactor portion of the FCC is where the cracking reaction takes place. In the riser, close contact with hot regenerated catalyst causes the feed to vaporize rapidly and rise. Cracking begins as soon as the vaporized hydrocarbon is adsorbed onto the catalyst. During cracking, carbon is deposited on the catalyst in the form of coke, deactivating the catalyst. By the time the vaporized charge reaches the reactor, the cracking process is virtually complete and the catalyst is spent.

Cyclonic separation is a method of removing particulates from an air, gas or liquid stream, without the use of filters, through vortex separation. Cyclones are used to prevent over-cracking by separating the spent catalyst from the hydrocarbon vapors. Cracked hydrocarbon vapors exit the top of the cyclones and are transported from the reactor to the main fractionator through the reaction mix line. Before leaving the reactor, spent catalyst passes through a stripper section in the reactor where any remaining adsorbed hydrocarbon is separated from the catalyst by using a combination of stripping steam and baffles/ shed trays.

Regenerator: The regenerator restores catalyst activity by burning catalyst coke deposits and provides the heat required by the endothermic cracking reaction. Regeneration temperatures are typically 650°C to 760°C. The regeneration process begins when spent catalyst from the reactor enters the regenerator through the spent catalyst standpipe. Air is used as lift gas to propel the spent catalyst up the standpipe into the regenerator. Once in the regenerator, the hot catalyst is contacted by oxygen and combustion begins. Coke is consumed in the combustion process.

Cyclone separators are used to disengage catalyst carried upward by rising flue gas. The flue gas escapes from the top of the cyclones into the flue-gas system. The recovered catalyst is directed down to the dense phase of the regenerator.

Flue-Gas System: The flue gas system is responsible for heat recovery and purifies regenerator waste gas for discharge to the atmosphere by cooling the gas, removing catalyst fines, and removing pollutants. Waste flue gas leaves the regenerator 675^0C to 760^0C. Flue gases are burned in a carbon monoxide (CO) boiler for further
heat recovery.

Fractionator: The main fractionator cools the cracked reactor effluent gas and separates the light and heavy cycle oils from the lighter fractions. Process flow diagram of FCCU is illustrated in Figure 1.

Materials of Construction: Common materials of construction in FCCU are:

- Carbon steel
- Alloy Steels (1-1/4 Cr ½ Mo, 5Cr1/2 Mo, 9Cr 1 Mo)
- Type 300 series stainless steel
- Type 400 series stainless steel
- Alloy 625 nickel-based alloy
- Refractory linings.

Typical Corrosion in FCC Unit

- High-temperature oxidation in 9cr 1Mo Heater Tubes
- Erosion- Corrosion in Catalyst section
- Sigma phase Embrittlement in Cyclones
- Stress Corrosion Cracking in SS 316 Heater Tubes
- Liquid Metal Corrosion in once observed in Orifice chamber caused by molten Aluminum cladding of external insulation accidently came in contact with SS 304 metallurgy of orifice chamber. It was a very isolated case study of failure as outlined below.

III. LIQUID METAL CORROSION

Liquid metal corrosion is simply a dissolution process of contaminant metal in contact with molten metal. A contaminant metal with higher solubility in the molten metal generally exhibits higher corrosion rate. In case of an alloy, the solubility

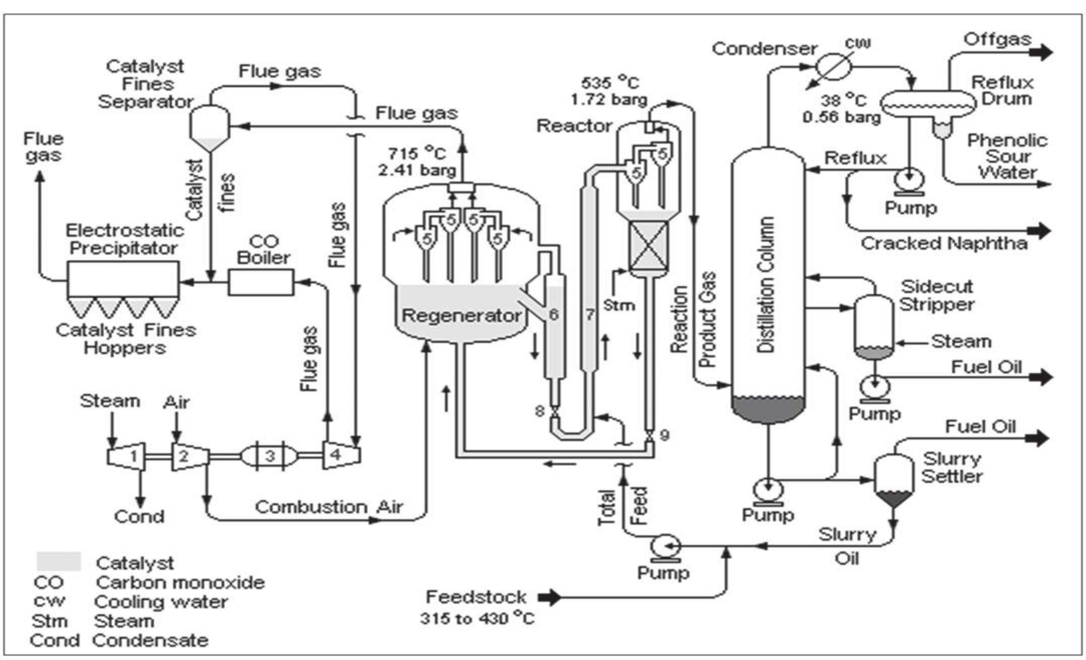

Figure 1. A schematic flow diagram of a Fluid Catalytic Cracking unit as used in petroleum refineries. Here 1: Start-up steam turbine, 2: Air compressor, 3: Electric motor/generator, 4: Turbo expander, 5: Cyclones, 6: Catalyst withdrawal well, 7: Catalyst riser, 8: Regenerated catalyst slide valve, 9: Spent catalyst slide valve.

of major alloying element determines the corrosion rate.

Increase in temperature increases the corrosion rate. Aluminum melts at 660^0C. Iron, Nickel and cobalt along with their alloys are readily dissolved by molten aluminum. This type of corrosion is very rare and occurs only if temperature goes high to melt the metal and molten liquid droplet comes in contact with other metal.

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Virendra Babu obtained B.Tech from Department of Metallurgical Engineering, Indian Institute of Technology, Kanpur in 1981 and joined Indian Oil Corporation as a Management Trainee. Served IOC for 34 years in various capacities, including Project Execution, Project Safety, ISO 9001 and other related ISO works, Senior Manager (M&I) Northern Region as HOD in Marketing Division and Manger M & I (May 1999-2008).

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