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Study on the Effects and Optimum Addition of Metal Passivation Additive in Fluidized Catalytic Cracking

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***Abstract* -- Nickel and Vanadium contents present in the Vacuum Gas Oil slowly got aggregated in Fluidized Catalytic Cracking catalysts. This will catalyze the undesirable dehydrogenation reaction. This reaction will mostly occur in the LPG stream, which results in the reduction of LPG yield and increase in gas production in the form of hydrogen, methane, ethane and coke yield. To control this undesirable reaction, an additive was proposed. This new additive was named generally as Nickel Passivator or Metal Passivator. This is an aqueous solution of Antimony Pent oxide (Or Bismuth), Phosphate salt and Tri-ethanol amine. By adding this, it will passive the effect of Nickel and Vanadium on catalysts, thereby, controlling this dehydrogenation reaction. The metal passivator addition rate was varied from 0 to 12 Kg/day. During this dosing period, off gas yield dropped, LPG yield was increased, Hydrogen content in off Gas yield reduced. The optimum Metal Passivator addition rate is 12 Kg/day. At this point, Nickel to Antimony ratio became constant at 7.5 Units**

Keywords – Dehydrogenation; Metal Passivation; Vacuum Gas Oil

I. INTRODUCTION

The Fluidized Catalytic Cracking (FCC) process converts heavy crude oil fraction into lighter, more valuable hydrocarbon products at high temperature and moderate pressure in the presence of a finely divided silica / alumina based catalyst. In the course of cracking large hydrocarbon molecules converted into smaller molecules, a non-volatile carbonaceous material, commonly referred to as coke, is deposited on the catalyst. This coke deactivates the catalytic cracking activity of the catalyst by blocking access to the active catalytic sites. In order to regenerate the catalytic activity of the catalyst, the coke deposited on the catalyst is burned off with air in the regenerator vessel.

One of the important advantages of fluid catalytic cracking is the ability of the catalyst to flow easily between the reactor and the regenerator when fluidized with an appropriate vapor phase. In FCC units the vapor phase, on the reactor side is vaporized hydrocarbon and steam, while on the regenerator side the fluidization media is air and combustion gases. In this way; fluidization permits hot regenerator catalyst to contact fresh feed; the hot catalyst vaporizes the liquid feed and catalytically cracks the vaporized feed to form lighter hydrocarbon products. After the gaseous hydrocarbons are separated from the spent catalyst, the hydrocarbon vapor is cooled and then fractionated into the desired product streams. The separated spent catalyst is transferred by fluidization from the reactor to the regenerator vessel where the coke is burned off the catalyst to restore its activity. In the course of burning the coke a large amount of heat is liberated. Most of this heat of combustion is absorbed by the regenerated catalyst and is carried back to the reactor by the fluidized regenerated catalyst to supply the heat required to drive the reaction side of the process. The ability to continuously circulate fluidized catalyst between the reactor and the regenerated allows the FCC to operate efficiently as a continuous process.

The objective of this study is to control the dehydrogenation reaction which is taking place in the Fluidized Catalytic cracking Reactor. Nickel and Vanadium contents present in the feed (Vacuum Gas Oil) slowly got aggregated in FCC catalysts. This will catalyze the undesirable dehydrogenation reaction in the reactor. This dehydrogenation reaction will mostly occur in the LPG stream, which results in the reduction of LPG yield and increase in gas production in the form of hydrogen (C1's, C2's and H2) and coke yield

To control this undesirable reaction, an additive was added. This new additive was named generally as Ni-Passivator or Metal Passivator. This is an aqueous solution of Antimony Pent oxide (Or Bismuth), Phosphate salt and Tri-ethanol amine. By adding this additive, this will passive the effect of Nickel and Vanadium on catalysts, thereby, controlling this dehydrogenation reaction.

In this project, a study was carried out on the effect of Metal - Passivator addition on feed on a Fluidized Catalytic cracker. Here, Nickel, Vanadium and Antimony content on the catalyst was analyzed before and after addition of additive. The result was shown how the additive has improved the LPG yield by suppressing the dehydrogenation reaction.

II. EXPERIMENTAL

A. *Experimental Procedure*

In this experiment, Metal Passivator was added to Reactor feed in various compositions (0 to 12 Kg/day). Metal Passivator is a water based compound. Hence, it was added to the feed VGO (Vacuum Gas oil) just before it enters the reactor, otherwise, it may conceal before it enters the reactor.

Addition of metal passivator was done through a standard pot. From the pot, it was pumped to the reactor feed using a positive displacement pump. Once it was added inside the reactor along with the VGO, the conditions were monitored. To preserve the accuracy of the result, major changes were avoided.

During this experimental period, Catalyst was analyzed for Nickel, Vanadium and Antimony content, LPG yield, off gas yield and hydrogen in off gas

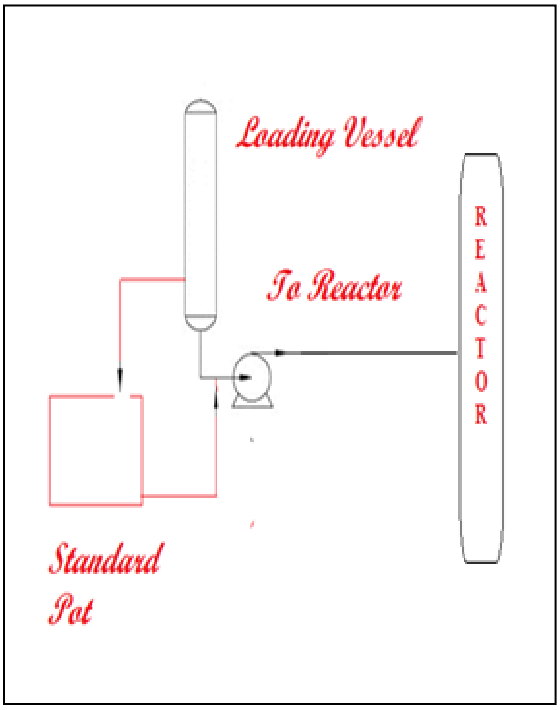

Fig. 1. Experimental set up

B. *Crudes Processed While Conducting Experiment*

The study was started on 20/01/2012 and concluded on 12/05/2012. During this period, four different crudes were processed. The period between which the crudes were processed are as follows

Crude 1: Iranian Mix + Ravva Crudes
Crude 2: Murban Crude
Crude 3: Merrilite Crude
Crude 4 : Ravva Crude

To analyze, the conditions monitored are Unit Feed Rate, Crude Processed, Reactor Temperature, Catalyst Circulation rate, LPG Yield and Off Gas Yield.

Spent catalyst and Off Gas samples were analyzed to find the Nickel, Vanadium and Antimony content in Spent catalyst and Hydrogen content in Off Gas

Nickel and Vanadium are catalytic poisons which are catalyzing the unwanted dehydrogenation reactions. Antimony is a passivator which suppresses the effect of Nickel and Vanadium. Hence, by monitoring the Nickel to Antimony Ratio and Vanadium to Antimony Ratio we can analyze, the quantity of metal passivator required to suppress the Dehydrogenation Reaction. Optimum addition of metal passivator is measured by monitoring the LPG and Off Gas yields. Our aim is to maximize the LPG yield and minimize the Hydrogen content in Off Gas yield.

C. *Results And Discussions*

This experiment was carried out by varying the addition of Metal Passivator to reactor. This quantity was varied between 0 to 12 Kg/day at different Crude types, Feed rates, Reactor Temperature. Data collected are LPG and Off Gas Yield, Hydrogen content in off gas, Nickel, Vanadium and Antimony content in catalyst.

Fig. 2, shows the effect of Ni-Passivator Addition to Reactor feed on Hydrogen Content in off Gas. Here, it was observed that, Addition of Ni-Passivator reduces the Hydrogen content in the Off Gas. If Ni-passivator addition was suspended, Hydrogen content is getting increased steeply. At the rate of 12 Kg/day of Ni-passivator, Hydrogen content is getting narrowed down

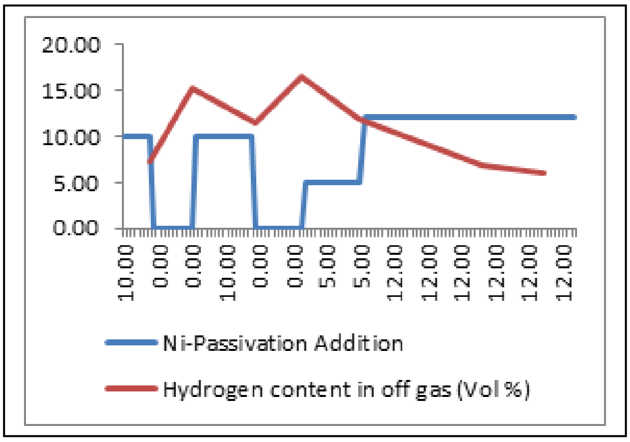

Fig. 2. Graph drawn between Ni-Passivator Addition to Reactor feed Vs Hydrogen Content in off Gas

Fig. 3, shows the effect of Ni-Passivator Addition to Reactor feed on antimony content on catalyst. Here, it was evident that, Addition of Ni-Passivator increases the Antimony content in the catalyst which can stop the de-hydrogenation reaction which is not preferable

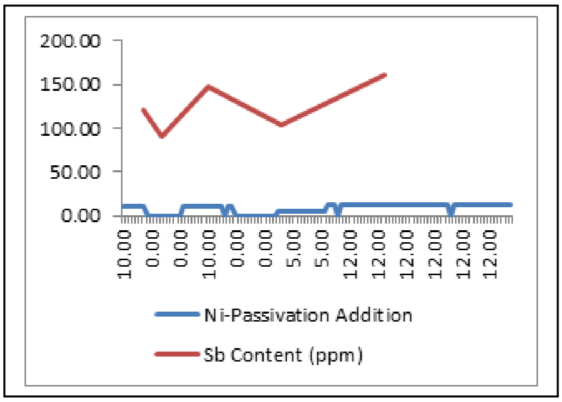

Fig. 3. Graph drawn between Ni-Passivator Addition to Reactor feed Vs Antimony Content in the catalyst

Fig. 4 shows the effect of Ni-Passivator Addition to Reactor feed on Nickel to antimony ratio. Here, it was observed that, Addition of Ni-Passivator reducing the Nickel to Antimony Ratio. At the rate of 12 Kg/day of Ni-passivator, Nickel to Antimony Ratio was almost steady at 7.5 Units

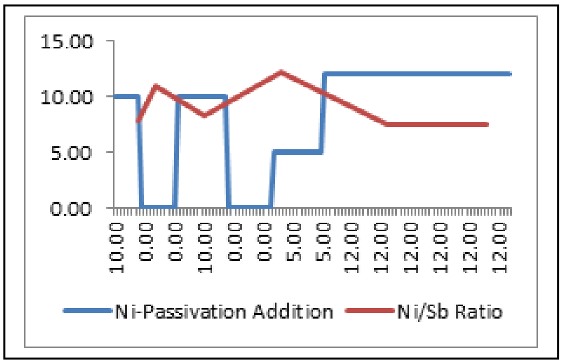

Fig. 4. Graph drawn between Ni-Passivator Addition to Reactor Vs Ni/Sb Ratio

Fig. 5 shows the effect of Ni-Passivator Addition to Reactor feed on Vanadium to antimony ratio. Here, it was evident that, Addition of Ni-Passivator reducing the Vanadium to Antimony Ratio. At the rate of 12 Kg/day of Ni-passivator, Vanadium to Antimony Ratio was almost narrowed down to 15 to 16 Units

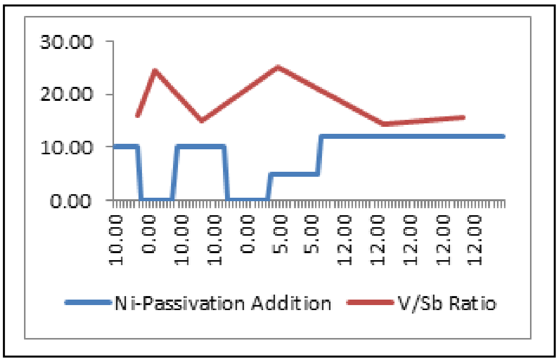

Fig. 5. Graph drawn between Ni-Passivator Addition to Reactor Vs V/Sb Ratio

Fig. 6 shows the effect of Ni-Passivator Addition to Reactor feed on LPG Yield. Here, it was observed that, Addition of Ni-Passivator increases the LPG Yield. It was also noted that, High LPG yield during Ravva crude processing and a steep drop in LPG yield due to Merrilite crude processing. It is because of the quality of the crudes processed. Merrilite crude composition shows LPG yield after cracking is comparatively less and for Ravva crude, it is relatively high. Here it was clearly observed a drop in LPG yield when there is no addition of metal passivator.

Demarcation was done for the different crude processed during the experimental period and was shown in the graphs below

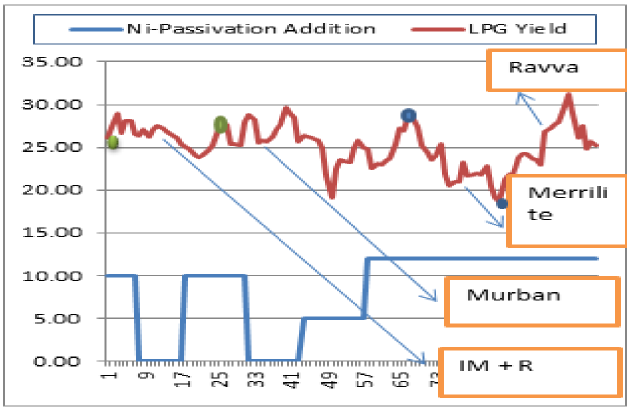

Fig. 6. Graph drawn between Ni-Passivator Addition to Reactor Vs LPG Yield

Fig. 7 shows the effect of Ni-Passivator Addition to Reactor feed on Off Gas Yield. Here, it was observed that, Addition of Ni-Passivator decreases the Off Gas Yield. The similar fashion of change in Off Gas was observed during Ravva and Merrilite crude

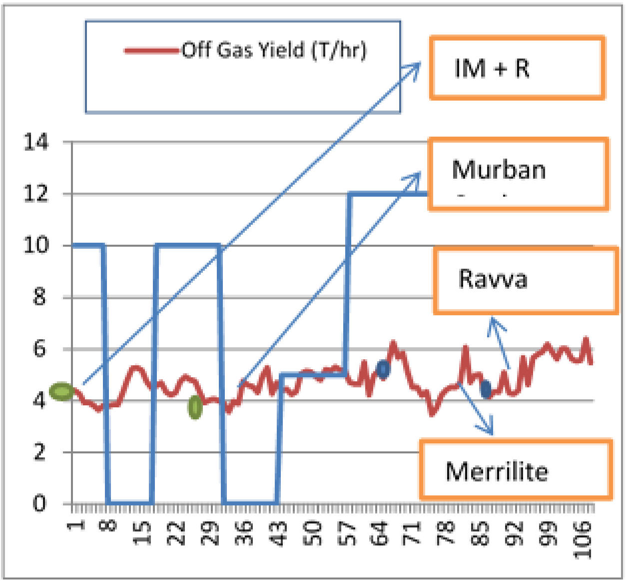

Fig. 7. Graph drawn between Ni-Passivator Addition to Reactor Vs Off Gas Yield

A Graph is drawn between Ni-Passivation addition against the LPG yield Raise or Drop. It shows raise in the LPG yield whenever Ni-passivator was added. Drop in LPG yield during Merrilite crude processing is the due to the crude quality

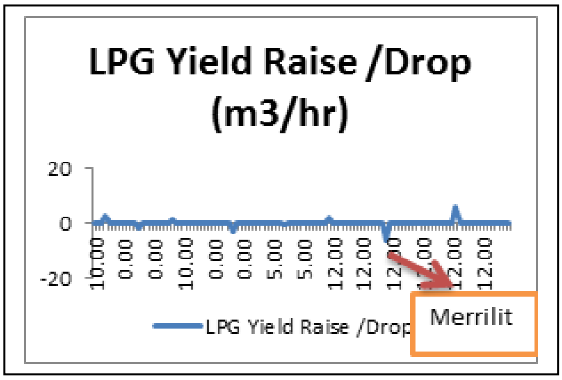

Fig. 8. Graph drawn to observe LPG Yield Raise / Drop.

A Graph is drawn between Ni-Passivation addition against the Off Gas yield Raise or Drop. It shows a drop in the Off Gas yield whenever Ni-passivator was added

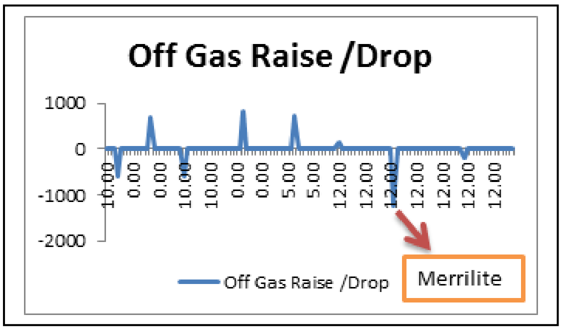

Fig. 9. Graph drawn to observe Off Gas Yield Raise / Drop

III. CONCLUSION

Antimony content in Metal Passivator suppresses the effect of Nickel to a great extent.
Whenever the Metal Passivator was added,

- When Metal Passivator addition rate was 12 Kg/day, Nickel to Antimony ratio became constant at 7.5 Units. Hence, further addition of passivator will not reduce the effect of Nickel. The analysis confirms that the optimum addition rate is 12 Kg/day
- Ni/Sb (Nickel to Antimony) ratio came down significantly. Variation Observed is ± 2 Units
- V/Sb (Vanadium to Antimony) ratio came down considerably. Variation Observed is ± 5 Units
- LPG yield is increased on an average of 1.55 m3/hr after the addition of Metal Passivation. This accounts to 6% raise in LPG yield
- Annual Recovery of LPG by using this optimum Metal Passivator is 13578 m3. This will provide an annual saving of 36.66 Crores (Cost of LPG: 1 Ton = Rs.45000)
- Hydrogen content in the off gas varied from 6.12 to 16.4 % (Volume %). Reduction of Hydrogen content in off Gas yield is 10%.
- The Hydrogen content allowed in Off Gas is only 25-30% (Maximum). This is due to the calorific value difference. (The Calorific Value for Hydrogen is 141790 kJ/kg. The Calorific Value of Off Gas is 78052 KJ/Kg). High calorific value will reduce the life of the Heater burners. By Reducing the hydrogen content in FCC off gas will increase the flexibility of mixing Hydrogen from the other treating units which will avoid flaring and pollution of atmosphere
- Without Metal Passivator off gas yield raise to a maximum of 807.98 Kg/hr. By its addition, the off gas yield reduced by 597.33 Kg/hr. This accounts to a off gas yield drop of 19.01%

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