

Study on Metal Passivation Additive in R-FCC and Their Effects

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Abstract: Metals are continuing to rise as we see increased residue processing as a global trend. Metal contaminations are harmful to the catalyst and can unwanted reaction in the R-FCC. Metal deposits on the catalyst and its effects on the catalyst activity. Practice on antimony metals passivation technology to the increase R-FCC unit oil feed capacity significantly decrease the yields of hydrogen and coke and increase the yield of gasoline and decrease coking reaction. Also improve economical benefits associated with passivation are heavy fuel oil product upgrading, feed stock selection, reduced catalyst selection, compressor duty and maintenance blower duty.

Keywords: Dehydrogenation, Metal Passivation, Vacuum Gas Oil, Kbc Petro SIM,

I. INTRODUCTION

The concept of Fluidized Catalyst Cracking (FCC) was developed during 1940's with powdered catalyst in fluidized condition. The first break through came when Y type Zeolite based catalyst was used instead of the alumina amorphous catalyst used during the 1950's. The extremely high active and lower coke forming tendency of zeolites catalyst led to many changes in the reactor configuration. The next breakthrough came during the mid 1960's, when USY based catalyst was introduced. These catalysts of high hydro thermal stability produced less coke and also increase the octane number of the gasoline. Then during the 1980's large number of additives like Nickel and Vanadium Passivator, CO combustion promoters and SOX emission controller and special additives for attrition resistance, octane improvement were developed to optimize the reaction.

Prior to the introduction of FCC unit, all the vacuum tower gas oil and visbreaker gas oil were blended with the fuel oil stream out thermally cracked to produce kerosene and gasoline. The sudden crude price hike in the beginning of 1970's influenced the introduction of FCC units all over the world and in Indian refineries too.

In thermal cracking, the selectivity of the product will be low and lighter components (< C3) production will be high. By FC one can get high yield

Of lighter products and less heavier components.

Also the high octane number which has become an important factor for gasoline quality can only be achieved by FCC. Though investment cost of FCC unit is high, the

increased yield of high quality products from FCC unit justifies for the installation of FCC unit.

Earlier in FCC it was only single catalyst regeneration system and later this has been changed to two stage regeneration system for reducing the catalyst deactivation rate and effective catalyst regeneration. In single stage regeneration catalyst will get deactivate very fast due to higher regeneration temperatures and presence of water vapors. In two stage regeneration system approximately 60 – 70% of the coke is burnt at mild condition in the first stage regenerator and the second stage regenerator completes the coke removal in an oxygen rich, higher temperature environment. Most of the hydrogen in coke is removed in the first stage itself at mild (low temperature) condition. Also the single stage regenerator vessel.

A. FCC has mainly three sections

- (1) Reactor and regenerator : the main objective of FCC unit is to catalytically crack the mixture of vacuum gas oil feed
- (2) Unsaturated gas separations unit : the function of unsaturated gas separations unit is to separate and recover hydrocarbon vapors and hydrocarbon liquid stream produced by cracking reaction in reactor
- (3) Flue gas desulphurization unit: the main objective of FGD unit is to treat the flue gases fluidized catalytic cracking unit to remove sulfur gas contain for the absorber of SO₂ into the scrubbing liquid.

II. METAL PASSIVATION:

Nickel deposited on the catalyst promotes dehydrogenation reactions and thus increases the tendency to form coke and H₂ during the FCC reactions. It can have a detrimental effect on both plant operation and reaction conversion. Ni Passivator, such as antimony and bismuth, can be used to reverse this negative effect by forming an alloy with the nickel to reduce the activity for dehydrogenation. The scale of reduction is a function of the concentration ratio between Passivator and Ni on the equilibrium catalyst. The effectiveness curve is modeled by the following equation.

$$f(Pa/Ni) = \frac{(XKUPa + Pa/Ni)^{-XKUPb}}{XKUPa^{-XKUPb}} \quad (1)$$

Where:

Pa/Ni = Concentration ratio of Passivator vs. nickel on equilibrium catalyst.

XKUPa = A constant value equal to 0.1 for passivation effect on coking and 1.0 for effect on H2 yield.
 XKUPb = Tuning parameter; XKUP2 (101) for effect on coking and XKUP2 (100) for effect on H2 yield.

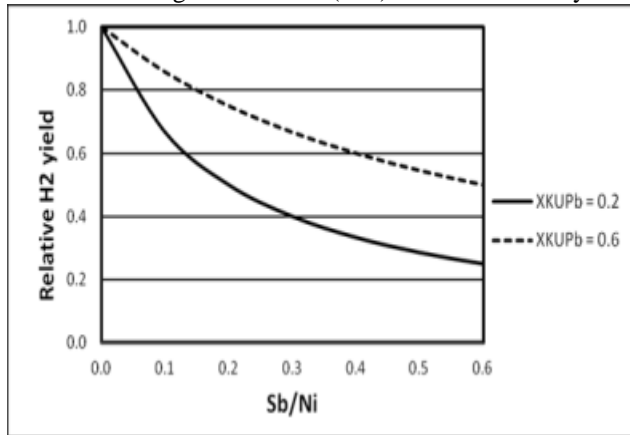


Fig. 1 (Ni Passivation Effect Curve)

III.SIMULATION:

A. SUMMARY OF FCC

The FCC unit simulation is based on physical and chemical principles, published correlations, and KBC-proprietary methods. Calibration factors are used to match test run data, and then are used to predict the effects of changes to that data.

When calibrating, the product yields and properties are used along with the data supplied to calculate the Calibration Factors. For some calculations, initial factors are assumed and the calculations are performed in an iterative procedure until a match is reached. In other cases the Calibration Factors are calculated directly. The final factors are displayed so they may be used in subsequent Predict runs, analyzed for model validation, or averaged with other Calibration Factors for Predict runs.

The Calibration run provides Calibration Factors for conversion, product yields, carbon-on-catalyst, and recycle property relationships. It calculates cracking rates, catalyst circulation, heats of combustion, rate constants for coke burning and regeneration afterburning, selected constraint values, and other operating variables.

When predicting the operation and economics of a FCC with given feed and set of operating conditions, the Calibration Factors are given as data inputs, and the model computes the yields and properties, closing on the heat balance, coke make (burn), and recycle properties.

In the Predict mode, FCC-SIM calculates values for all dependent variables such as conversion and product yields. You have many options for selecting which variables are fixed and which are calculated, so you can use the program for a wide variety of problems. For example, effects of changes in feed qualities and rates, riser outlet temperatures, feed preheat, recycle rates, regenerator steam and water rates, product cutpoints, etc., can be evaluated in terms of product yields and qualities.

A. CONVERSION

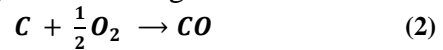
In the reactor, gas oil and resid feeds are converted to lighter products (light gas oil, naphtha, gas) and coke. There is a net conversion of naphthenes to aromatics, and the olefins formed are partially saturated. Conversion is calculated as conversion to a standard 430°F (221°C) cutpoint, which is adjusted for naphtha cutpoint.

B. Regenerator Calculations

The regenerator model simulates the burning of coke to produce CO, CO₂, H₂O, SO₂, and SO₃ to meet the carbon-on-regenerated catalyst target. The flue gas leaving the bed is subject to further conversion of CO to CO₂ (afterburning) depending on the O₂ concentration, CO concentration, and temperature. Introduction of steam and water sprays into the dilute phase and plenum of the regenerator enter into the heat balances to reduce the temperatures and thus lower the afterburning reaction rates.

In each regenerator stage, the dense bed reactions are:

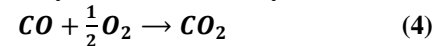
Primary coke burning reaction



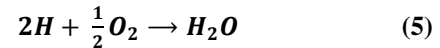
Secondary coke burning reaction



Promoted by metals on catalyst



H₂ in coke

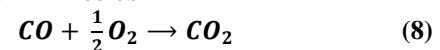


Sulfur components are assumed to react to form products of SO₃ and SO₂:



The dilute phase and plenum reaction is:

Afterburn kinetics



C. Feed Characterization

The sequence of feed characterization and blending can be summarized as:

Determine the concentrations of each quality for each fresh feed.

Determine the carbon number distribution of pseudocomponents that approximate each fresh feed and assign concentrations of each key quality to each carbon number present.

If more than one feed is involved in the simulation, the feeds physically mixed together are blended by carbon number, resulting in a single component feed by carbon number.

Each feed is broken down into carbon number pseudocomponents with the following rate and property information determined. They are very important in the kinetic reaction calculations.

Weight rate, lb/hr

Volumetric rate, barrels/hr

Molar rate, moles/hr
Boiling point, degrees F
Specific gravity
Characterization factor
Molecular weight
CA, CN, CP, weight fraction
Breakdown of total CA into one-ring, two-ring, three-ring and four plus-ring aromatics, weight fraction
Olefin content, the number of C=C bonds/carbon atom

D. FCC Reactor

The reactor is divided into three zones.

Riser – Where the feed mixes with regenerated catalyst and enters the reactor vessel.

Dense Bed – Where the reacted feed from the riser enters a dense, back-mixed bed of catalyst containing the average outlet coke-on-catalyst.

Dilute Phase – Where the reacted feed from the riser or dense bed (if there is one) undergoes further conversion in the presence of low catalyst density.

The reactions are modeled separately for each zone using the same reaction scheme. The reaction network is constructed on the basis of 80 carbon pseudocomponents. Fundamental kinetic principles of FCC reactions are applied in the rate expressions. The extent of a reaction in each of these three zones is determined by the reaction conditions at each zone. The main factors that differ most between the three zones are the contact time between oil mixture and catalyst, catalyst activity, reaction temperature and reactivity of the oil mixture.

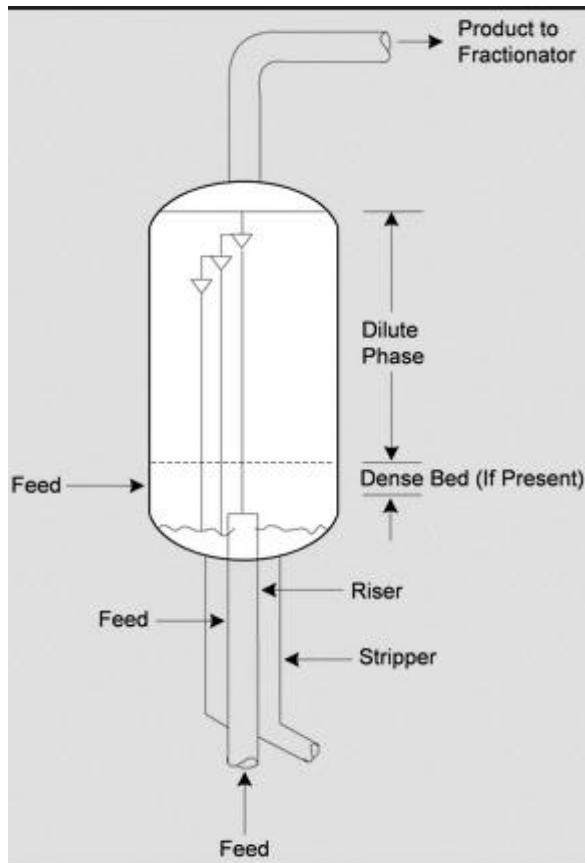


Fig. 2 (Schematic Diagram of Regenerator)

E. Regenerator Model

The regenerator model calculates the reactor/regenerator heat balance. This portion of FCC-SIM determines the heat from burning coke, the resultant regenerator temperatures, the required air rate, the flue gas composition, and carbon-on-regenerated catalyst.

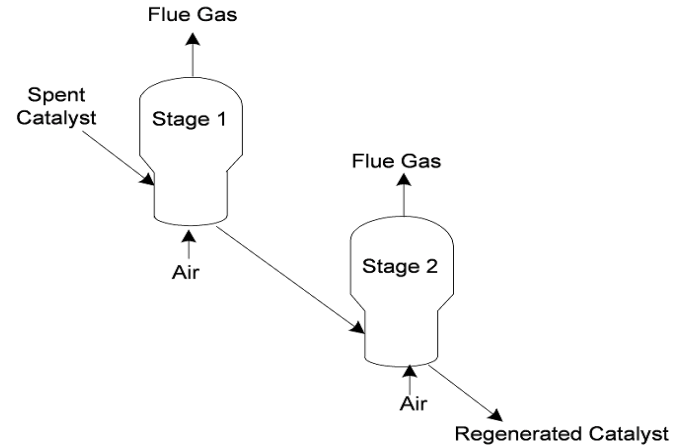


Fig. 3 (Two Stage Regenerator)

the regenerator model is turned to match observed regenerator performance by the calculation of Calibration Factors. In particular, Calibration Factors are calculated to force theoretical coke burn kinetic expressions to match the observed coke burn based on key input data as follows:

1. Carbon on regenerated catalyst (CRC)
2. Dense phase temperature
3. Flue gas temperature and composition
4. Air rate
5. Dense phase catalyst inventory
6. Heat losses
7. Steam and condensate quenches
8. Air temperature and composition
9. Physical dimensions.

For a two-stage regenerator, this data for both stages over specifies the calibration calculations. When the two-stage regenerator is calibrated, the input values for the first stage CRC and dense phase temperature are ignored and replaced with calculated values.

The calculated values for the first stage CRC and dense phase temperature are based on heat and material balances in the following sequence of steps:

1. Total coke burn rate is calculated from flue gas compositions and air rates at both stages.
2. Catalyst circulation rate is calculated from overall heat balance around both stages combined.
3. First stage CRC is calculated from the second stage coke burn rate, second stage CRC and catalyst circulation from (2) above. This CRC includes residual sulfur and hydrogen not burned off in the first stage.
4. First stage dense phase temperature is calculated from heat balance around the isolated first stage.

At this point, the Calibration Factors for both stages are calculated using the calculated first stage CRC and dense phase temperature values for the first stage Calibration Factors.

Finally, the technique used in making predictions for a two-stage regenerator system is similar to the single stage technique with the following constraints:

- The first stage must be a partial burn or oxygen starved mode of operation.
- The second stage must be a complete burn or excess oxygen mode of operation.

IV. SCREEN SHOT OF FCC IN PETRO SIM

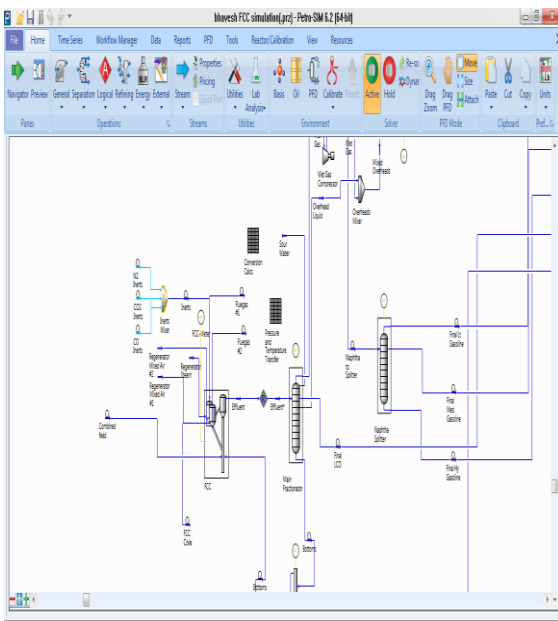


Fig. 4 (Screen Short of Petro-SIM Overall FCC)

V. CONCLUSION

I run this simulation with Ni passivation and Without Ni Passivation (with same and different feed properties)

A. With Ni passivation:

Increase Gasoline product and LPG and reduced off gases and also reduce catalyst selection, compressor duty and maintenance blower duty.

DRY GAS PROPERTIES:

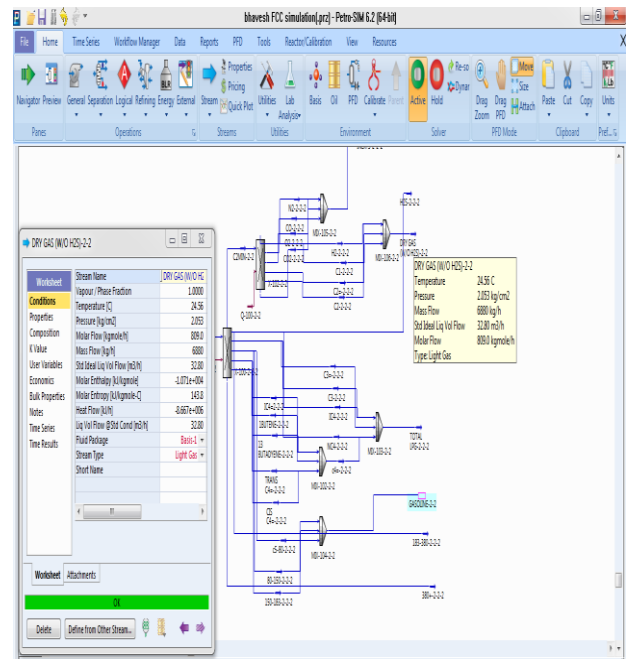


Fig. 5 (Screen Short Of Dray Gas)

TOTAL LPG:

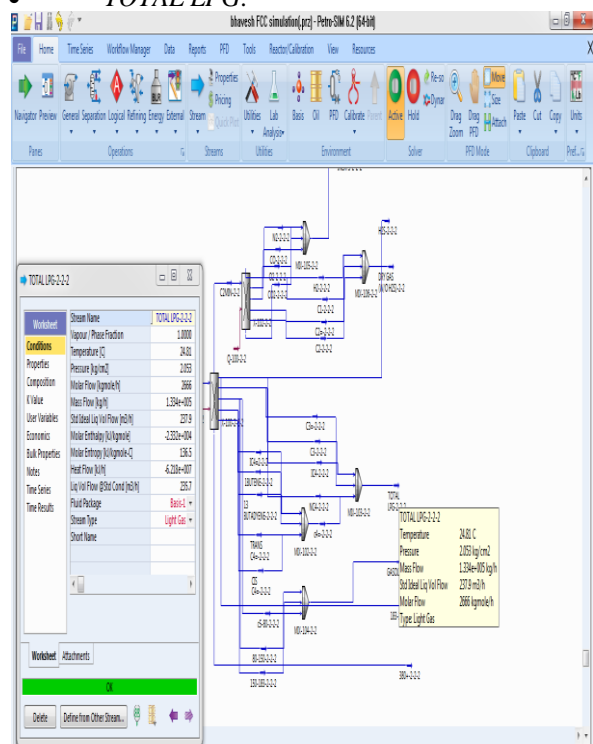


Fig. 6 (Screen Short of Total LPG)

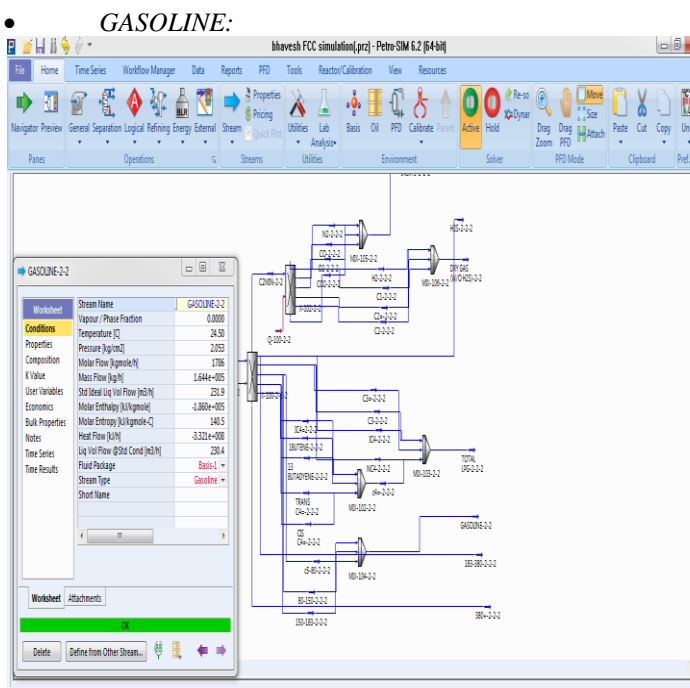


Fig. 7 (Screen Short of Gasoline)

VI. REFERENCES:

1. Study on the Effects and Optimum Addition of Metal Passivation Additive in Fluidized Catalytic Cracking (A. Ramanathan)
2. Reducibility of metals on fluid cracking catalyst (W.-C. Cheng, M.V. Juskelis and W. Suarez)
3. Iron Contamination Mechanism and Reaction Performance Research on FCC Catalyst (Zhaoyong Liu, 1,2 Zhongdong Zhang, 1,2 Pusheng Liu, 2 Jianing Zhai, 2 and Chaohe Yang 1)
4. Role of nickel on vanadium poisoned FCC catalyst: A study of physicochemical properties (U. J. Etim a , B. Xu a , P. Bai a , Rooh Ullah a , F. Subhan a , b , Z. Yan a , *)
5. A. Ramnathan, (2015). Study on the Effects and Optimum Addition of Metal Passivation Additive in Fluidized Catalytic Cracking. International Journal of Engineering Research & Technology (IJERT)
6. W.-C. Cheng et al, (1993) Reducibility of metals on fluid cracking catalyst. Elsevier Science Publishers B.V., Amsterdam
7. A.A. Lappas, L. Nalbandian, D.K. Iatridis, S.S. Voutetakis, I.A. Vasalos (2001). Effect of metals poisoning on FCC products yields: studies in an FCC short contact time pilot plant. Chemical Process Engineering Research Institute (CPERI) and Department of Chemical Engineering University of Thessaloniki.
8. LI Jian-zhong, HUANG Jiu-gui, TIAN Yan-wen, LIU Chang-sheng, (2007). Corrosion action and passivation mechanism of magnesium alloy in fluoride solution. sciencedirect.com
9. Zhaoyong Liu, Zhongdong Zhang, Pusheng Liu, Jianing Zhai, and Chaohe Yang, (2015). Iron Contamination Mechanism and Reaction Performance Research on FCC Catalyst. Hindawi Publishing Corporation Journal of Nanotechnology
11. Ocelli; Fluid Catalytic Cracking II ACS Symposium Series; American Chemical Society: Washington, DC, 1991.