Additive solution in FCC and RFCC: Propylene rich LPG and lower bottom

A.V.Karthikeyani*, B.Sarkar, B.Swamy, K.M.Prabhu and S.Rajagopal

Indian Oil Corporation Limited, R&D Centre, Faridabad, India.

Abstract

Fluid catalytic Cracking (FCC) is an important secondary refining process for bottom of barrel up-gradation as well as to produce valuable lighter products such as high octane gasoline and light olefins. This process is the second largest propylene production source after steam cracking, producing about one third of the world propylene demand. Due to a steady increase in the demand for propylene, FCC has become an important workhorse in improving the propylene yield. An economic analysis published in recent literature reports that this process will be more profitable in an integrated refinery-petrochemical complex. New FCC processes, revamp ideas, new catalyst formulations, and additives are some of the options, in general, available to refiners to increase propylene yield in a FCC unit. Among all these options, easiest, fastest and cheapest way to enhance propylene production while minimizing unwanted bottom is the use of ZSM-5 additives in FCC. In this endeavor, IOC R&D has developed a series of ZSM-5 additives for different process conditions and feedstock. Employing elaborate experimentations and excellent knowledge bank, optimal concentration of ZSM-5 and operating window for a particular feedstock are identified for maximizing propylene/LPG/lower bottom in RCC & FCC units This article describes the importance of using ZSM-5 additive in existing FCC & RFCC units, as an economical option to increase propylene yield.

Key words: FCC, RFCC, ZSM-5 additive, LPG, Propylene, bottom upgradation

1. Introduction

Fluid Catalytic Cracking (FCC) is an important secondary refining process in a modern refinery for upgrading vacuum gas oils and works in presence of fine zeolitic catalyst particles in a circulating and self heat balanced fluid bed reactor / regenerator system. FCC unit is operated to maximize the production of gasoline and diesel. However, in the recent past, FCC is being reoriented for maximizing yield of light olefins, where the main products are C3-C4 hydrocarbons for use as petrochemical feed stock. Customized new FCC processes, hardware revamp ideas, new catalyst formulations and additives are some of the options to increase propylene yields in FCC unit [1]. New FCC processes and revamp ideas for increasing propylene yield in FCC unit are not only cost effective but are the best solution for overcoming limitations in traditional FCC/RFCC units. In revamp cases and installation of new RFCC process options, the most handy tool has been liberal use of ZSM-5 additive. This is not only cost effective way for maximizing the propylene yield but also offers flexibility in restoring base performance with termination of usage of additive. Use of ZSM-5 additive, also improves octane number of gasoline.

*Corresponding author

Email address: karthikeyaniav@iocl.co.in

Generally, ZSM-5 additives are produced employing template /non-template zeolite bonded with clay-phosphate binder [2]. ZSM-5 additives are available as commercial product from various vendors with varying zeolites concentration bonded with proprietary binders and matrix.

This paper compares the activity and LPG/Propylene selectivity of additives prepared at IOC R&D with varying zeolites content, employing proprietary technology and at different additive concentration in base FCC / RFCC catalyst. This paper also discusses the optimal concentration of ZSM-5, process operating window, feed stock effects with special emphasis on maximizing propylene/LPG/lower bottom within the RCC & FCC units constraints.

2. Experimental

2.1. Feedstock

In this study, four types of feeds are used – Feed 1 is VGO , Feed 2 is Hydrotreated VGO for FCC units and Feed 3 and 4 are resids used in RFCC units and their major properties are given in Table 1.

Table 1
Properties of feed employed for catalyst performance

Feed type/No Properties	Feed 1	Feed 2	Feed 3	Feed 4
Density, gm/cc	0.910	0.898	0.866	0.936
Sulfur,wt%	0.80	0.32	0.71	2.54
CCR,wt%	0.65	0.30	1.50	2.80
Ni, PPM	1.64	<1	6.0	3.5
V,PPM	3.96	<1	16	5.0

2.2. Catalyst preparation

ZSM-5 additives were prepared at IOC R&D from precursor slurry using proprietary clay-phosphate binder and matrix with varying ZSM-5 zeolite content. The final slurry was spray dried in a conventional spray dryer fitted with two fluid nozzles in counter current mode of operation. The spray dryer products were calcined and characterized for physico-chemical properties.

2.3. Physico chemical properties

The ZSM-5 additives (Additive A, Additive B, and Additive C) were tested for physico – chemical properties such as surface area, pore volume, percent crystallinity, attrition resistance, apparent bulk density, particle size distribution and chemical composition (Table-2) as preliminary screening of additives can be done from these physico – chemical properties.

Table 2
Physico Chemical Properties

Properties	Additive-A	Additive-B	Additive-C
Zeolite content	low	medium	high
Surface area, m2/gm	60	75	148
Pore Volume, cc/gm	0.341	0.321	0.35
Attrition Index	3.2	4.5	4.51
APS, micron	90	87	90
Apparent Bulk Density, gm/cc	0.75	0.78	0.76
% Crystallinity	10-15	20-25	35-40

2.4. Pretreatment of fresh FCC / RFCC catalyst and ZSM-5 additives

Laboratory testing protocol comprises of two major steps viz., steam deactivation with / without metals and performance evaluation which include testing in a Micro Activity Test (MAT) unit followed by prediction of comparative performance of the catalyst and additive systems for the concerned commercial plant.

The feed processed in some of the Indian FCCUs contain very less contaminant metals (Nickel and Vanadium) so that metal on equilibrium catalyst (E-cat) is in the range of 2000 – 3000 ppm (Ni + V). Therefore, the metal free catalyst / additive steam deactivation protocol was followed. The metal free catalyst / additive deactivation was accomplished by steam treatment at elevated temperature to simulate the hydrothermal deactivation, which occurs in a commercial regenerator. Steaming conditions were typically chosen to achieve MAT activity, surface area and zeolite unit cell size close to the E-Cat properties of reference unit. However, since resid FCCUs process high Conradson Carbon Residue (CCR) feed containing more contaminant metals, this will lead to a significantly higher metal level on the E-Cat. i.e. > 3000 ppm (Ni+V). For evaluating catalyst/additive systems for these units, catalyst / additive deactivation is carried out in presence of metals. Requisite metals were loaded by Mitchell method, H2 reduced and steam deactivated.

Identical pretreatment was performed on the base catalyst system which was in use in the reference refinery for which performance prediction of the newly developed additives were tested and compared.

2.5. Simulated micro activity test (MAT)

An activity measurement for all the catalyst systems was done in ACE unit supplied by Kayser Technologies, USA. The experiments were carried out at three different cat/oil ratios by varying the amount of catalyst loading (with & without additive) at constant feed rate and feed injection time. The feed injection time was such that it minimized the effect of time averaging on yields because of catalyst deactivation due to coke. Reaction operating temperature was maintained close to the riser outlet temperature in the commercial plant. After the completion of the reaction, the catalyst was stripped by nitrogen to remove adsorbed reaction products. Coke on catalyst was determined by in-situ regeneration at about 650 ^{0}C with fluidized air. The gaseous sample was analyzed online by a Micro GC, manufactured by M/s Agilent. The H2, C1, C2, C3, C4 and C5 lump was determined quantitatively. The liquid products were diluted in CS_2 solvent and analyzed in a simulated distillation analyzer manufactured by Perkin Elmer. The percentage of the liquid products boiling in the range of gasoline (C5-150^{0}C), heavy naphtha (C150-216 ^{0}C), Light Cycle Oil (C-216 ^{0}C -370 ^{0}C) and Clarified Oil (CLO) was calculated. Carbon on catalyst was determined by online IR analyzer.

2.6. Heat balanced performance prediction for the commercial unit using FCC model

The data analysis was done to compare

- Conversion data at constant severity
- Coke yield at constant severity
- Yield data at constant conversion

The coke yield and conversion at a severity (W/F) same as that of base case was calculated from the above correlations. Then the factors were calculated as follows:

$$\text{Coke factor} = \left.\frac{\text{Coke yield with catalyst along with additive}}{\text{Coke yield with base catalyst}}\right| \text{at base W/F}$$

$$\text{Conversion factor} = \left.\frac{\text{Conversion with catalyst along with additive}}{\text{Conversion with base catalyst}}\right| \text{at base W/F In}$$

addition, the following selectivity deltas (differences) were also calculated:

Delta Dry gas = Dry gas yield of catalyst along with additive – Dry gas yield with base catalyst at base conversion. Similar delta values were defined for the other yields (LPG, gasoline, HN, LCO & CLO). The data generated from simulated MAT was fed to the in – house developed FCCMOD simulator for performance prediction and comparison at the commercial level e.g. accounting of heat balance effect etc.

3. Results and discussion

3.1. Effect of ZSM-5 additive concentration

Evaluation experiments were conducted with base catalyst along with ZSM-5 additive-B (2 wt% and 4 wt% concentration) in presence of VGO feed stock (Feed 1) and the results are given in Table-3. With the increase in additive concentration from 2 wt% to 4 wt%, LPG yield has increased from 22.39 wt% to 23.7 wt% with the decrease in gasoline and TCO yields. Bottom yield is decreased from 8.89 wt % to 8.23 wt%. Propylene selectivity in LPG has gone up from 27 wt% to 32 wt%. With the same ZSM-5 concentration i.e. 4 wt%, if the type of feed stock is changed to hydrotreated VGO type (Feed 2), then the LPG yield increased from 23.7 wt% to 27.1 wt%. Bottom yield decreased from 8.23 wt% to 6.68 wt%.

Change of feed also enhanced propylene in LPG from 32 wt% to 33.5 wt%.

Table 3
Effect of ZSM-5 Additive concentration at constant coke

	ZSM-5 B	ZSM-5 B	ZSM-5 B
Feedstock	Feed 1	Feed 1	Feed 2
Catalyst composition, wt%	98	96	96
ZSM-5 additive concentration, wt%	2	4	4
ROT, ^{0}C	534	534	534
Dense bed temp. ^{0}C	710	713	685
Yields, wt%			
Dry gas	3.32	3.7	3
LPG	22.39	23.7	27.1
Gasoline	34.73	34.4	34.3
TCO	25.70	25	23.95
CLO	8.89	8.23	6.68
Coke	4.97	4.97	4.97
Propylene in LPG, wt%	27	32	33.5

3.2. Effect of ZSM-5 additive with different zeolite concentration

The base catalyst and additive were metal doped (Ni-3500 ppm & V-6500 ppm) as per the method described above in the pretreatment step 2.4. Performance evaluation of additives at identical concentration (15 wt%) in base catalyst, but with varying zeolite content in additives was carried out. The Feed 2 was used in the experiment. The results are compared with the base catalyst and are given in Table- 4. LPG yield increased from 23.81 wt% to 33.4 wt% with the decrease in gasoline yield from 38.9 wt% to 37.2 wt%. ZSM-5 additive has much lower potential to crack paraffins in the C5-C8 range and therefore unless reaction temperature is raised, it will crack saturated gasoline only to a small extent [4-5]. Propylene yield with respect to feed increased from 8.7 wt% to 11 wt%. With the increase in zeolite content in the additive, bottom (370 ^{0}C +) yield decreased from 4.73 wt% to 4 wt%. While selecting ZSM-5 additive with the objective to increase propylene and / or LPG yield for any unit, it is essential to see other hardware or process related constraints of the commercial plant. For example, in the reference case unit, as can be seen from Table 4, the plant can handle only a certain level of LPG & dry gas yield as there is a constraint in Wet Gas Compressor (WGC) capacity (i.e. Max of 54000 Kg/hr). Therefore, with this in mind, the ZSM- 5 additive 'A' was selected as a suitable additive for this RFCC unit.

Table 4
Effect of ZSM-5 additive at different zeolite concentration at constant coke

	Base catalyst	ZSM-5 A	ZSM-5 B	ZSM-5 C
Metals, PPM				
Ni	3500	3500	3500	3500
V	6500	6500	6500	6500
Feed	Feed 2	Feed 2	Feed 2	Feed 2
Catalyst composition, wt%	100	85	85	85
ZSM-5 Concentration, wt%	0	15	15	15
ROT, ^{0}C	511	511	511	511
Dense bed temp.^{0}C	643/696	664/719	669/722	671/727
<u>Yields, wt%</u>				
Dry gas	2.37	3.5	3.55	3.6
LPG (33% Max)	23.81	30.9	32.14	33.4
Gasoline (49% Max)	46.8	38.9	37.9	37.2
TCO	16.99	17.2	16.95	16.5
CLO (1.5% min-8.7 nmax)	4.73	4.2	4.16	4
Coke	5.3	5.3	5.3	5.3
Propylene, wt%	8.7	9.9	10.15	11
WGC load, Kg/hr (Max 54000 Kg/hr)	51243	53843	55753	57424
MAB, Kg/hr (Total)	55611	61000	61000	61000

3.3. Effect of ZSM-5 additive with different temperature

Experiments were conducted with ZSM-5 additive 'C' with the concentration of 30 wt% along with the base catalyst containing bottom upgradation component. Feed 1 was used in the experiment. Experiments were conducted at 550 ^{0}C, 580 ^{0}C, 600 ^{0}C and 650 ^{0}C reaction temperatures. The yields of dry gas and LPG with respect to conversion are plotted and shown in Figure-1 & Figure-2. With increase in reaction temperature from 550 ^{0}C to 600 ^{0}C, the drygas yield increased exponentially (Figure-1). The maximum propylene yield of 24 wt% is obtained at a reaction temperature of 580 ^{0}C however further increase in temperature resulted decrease in propylene yields (Figure-2). Therefore, it is concluded that for obtaining highest propylene yield, optimum temperature and ZSM-5 additive concentration is essential.

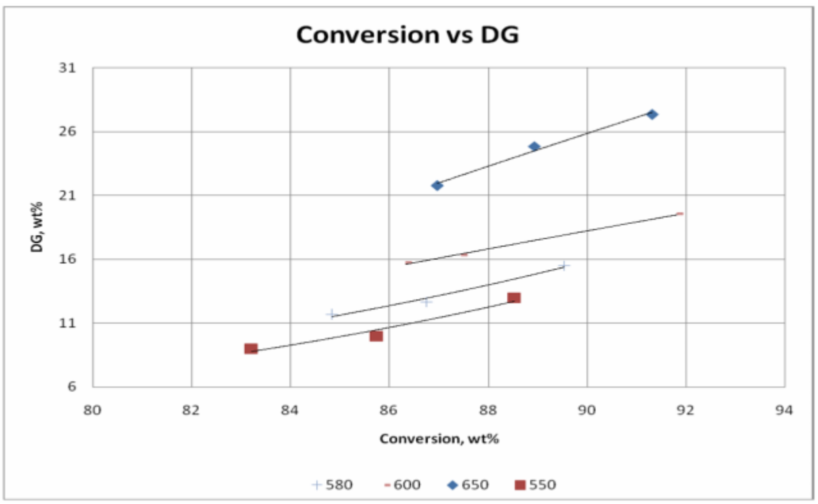

Fig. 1: Conversion vs drygas yield

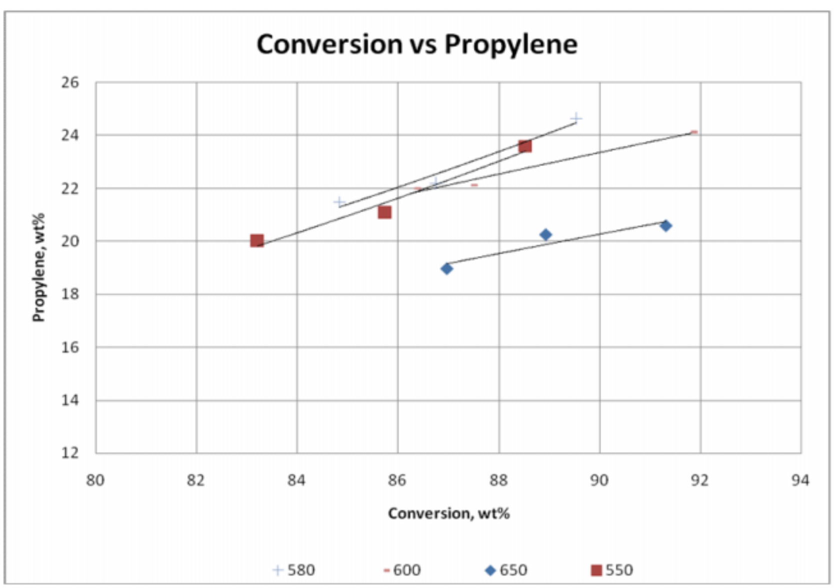

Fig. 2: Conversion vs propylene yield

3.4. Effect of commercial ZSM-5 additives on Propylene /LPG yield

Base catalyst and commercial ZSM-5 additives were metal doped (Ni-4000 ppm & V-5000 ppm) as per the method given above in the pretreatment step 2.4. The ZSM-5 additives were mixed with the base catalyst at 5 wt% concentration level. Feed 4 was used in this experiment. From the Table-5, it can be seen that commercial additives with different zeolite content produced LPG yield in the range of 14 -20 wt% and propylene yield of 4.5 – 7.1 wt%. Commercial additive C5 produced a maximum LPG (20.18 wt%) and propylene yield (7.1 wt%) at the cost of gasoline. However IOC R&D developed catalyst A produced LPG yield of 15.99 wt% mainly at the cost of bottom. Catalyst A produced higher valuable liquid products (Gasoline, Heavy Naphtha and LCO) and lower bottoms compared to C5. Therefore while selecting ZSM-5 additive for maximizing LPG & propylene yield, it is essential to see other yields such as gasoline, TCO & CLO, so that the overall techno economics is beneficial.

Table 5
Performance prediction of commercial ZSM-5 additives at constant coke

	Base catalyst	ZSM-5 (C1)	ZSM-5 (C2)	ZSM-5 (A)	ZSM-5 (C4)	ZSM-5 (C5)	ZSM-5 (C6)
Catalyst composition, wt%	100	95	95	95	95	95	95
ZSM-5 Concentration, wt%	0	5	5	5	5	5	5
ROT, deg.C	510	510	510	510	510	510	510
Dense bed temp. deg.C	642/707	638/700	638/700	638/699	639/701	642/706	642/706
Feed	Feed 4	Feed 4	Feed 4	Feed 4	Feed 4	Feed 4	Feed 4
Yields, wt%							
Dry gas	5.09	5.25	5.55	5.33	5.74	5.77	5.63
LPG	12.64	14.72	16.79	15.99	17.12	20.18	15.59
Gasoline	11.76	11.79	10.64	11.05	9.85	7.99	10.42
Heavy naphtha	15.52	15.09	14.17	15.82	13.22	12.65	14.41
LCO	40.84	39.89	39.71	41.15	39.99	40.46	41.67
CLO	8.49	7.6	7.48	5	8.42	7.29	6.62
Coke	5.66	5.66	5.66	5.66	5.66	5.66	5.66
Propylene,	3.8	4.5	5.0	4.79	6.2	7.1	4.75
WGC load, Nm^3/hr	24541	25471	27813	26663	28542	30870	27086

4. Conclusion

IOC R&D has developed a series of ZSM-5 additives and has conducted extensive studies in laboratory to explore the optimal concentration of ZSM-5, operating window, feed stock effects with special emphasis on maximizing propylene/LPG/lower bottom in FCC & RCC units. ZSM-5 additive is commonly introduced in the FCC/RFCC units as a separate additive which may comprise about 5-30 wt% concentration in the total catalyst inventory. It is possible to produce about 24 wt% of propylene on fresh feed basis in existing FCC /RFCC units at optimized ZSM-5 additive concentration and at reaction temperature within the unit hardware & operating constraints. It is also possible to maximize LPG/Propylene/other yields for a particular FCC / RFCC unit by employing ZSM-5 additives to maximize the Refinery margin.

Acknowledgement

The authors would like to thank P. K. Kasliwal (IOCL R&D) for carrying out activity evaluation, M. B. Patel & J. Christopher (IOCL R&D) for XRD measurements. The authors are also grateful to the management of R&D Centre, Indian Oil Corporation, Faridabad for the permission to publish this work.

References

[1] Mohammad A.Abul-Hamayel, Abdullah M.Aitani and Mian R.Saeed, Chem.Eng.Technol. 28, (2005) 923.

[2] Edward J. Demmel, U S Patent 5,190,902 (March 2, 1993).

[3] A . A i t a n i , T.Yoshikawa, T.Ino, Catalysis Today 60 (2000) 111.