ChemTech

International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.1, No.3 , pp 544-548, July-Sept 2009

MICRO SIMULATION STUDIES ON COKED FLUID CATALYTIC CRACKING CATALYST

M.Rajasimman* and M.Prabhakaran

Department of Chemical Engineering, Annamalai University, Annamalai nagar – 608002, Tamilnadu, India

Email: raja_simms@yahoo.com : cell: +91 9842565098

Abstract: In this work, a study was carried out in a Micro Activity Testing (MAT) unit for simulating the concept of partial recycling of the spent catalyst from reactor stripper. The physico-chemical characteristics of Unclarified Oil (UCO) and the properties of Equilibrium catalyst [E-cat] from the commercial Fluidized bed Catalytic Cracking (FCC) unit were studied. Spent catalyst was blended with the regenerated equilibrium catalyst from commercial unit in different proportions. The blended catalyst was evaluated in the MAT unit using UCO feed. The effect of 10%, 30 % and 50% (wt) of E-cat and spent catalyst and carbon to oil ratio (C/O) was studied using MAT unit with UCO. The yield pattern was compared for various catalyst combination of Ecat + spent catalyst at constant conversion 91. With spent catalyst in the blend the light gas (LG) yield decreases, with increase in C/O ratio. There is no significant change in bottoms (residue) yield, while there is a decrease in the diesel when C/O ratio is increased from 4.0 to 6.0. There is a significant increase in propylene yield when C/O ratio increases. The yield of isobutylene also increases when spent catalyst is procured along with regenerated catalyst.
Keywords: Catalytic cracking, E-cat, Fluidized bed, MAT unit, Spent catalyst, Unclarified oil.

1. Introduction

The fluid catalytic cracking (FCC) unit is the most important part of an oil refinery as it converts low value heavy hydrocarbon to more value gasoline diesel, oil and light olefins. The FCC has many advantages like greater LPG and gasoline yields, clear products with high yields, better production of aromatics, heat evolved in the regeneration of the catalyst is efficiently used, catalyst regeneration temperature is well controlled etc[1]. In recent years, in order to solve the problem that the feed stock has became heavier, producing more coke and to guarantee optimal yield and qualities of the environmentally acceptable traffic fuels, petroleum companies and academic institution have carried out further studies[2,3,4,5]. Wallenstein[6] has attempted prediction of yield patterns of different FCC feed stocks based on hydrocarbon types present in the feedstock. The present work is aimed to investigate the characteristics of Equilibrium catalyst [E-cat] and feedstock from the commercial FCC unit, blending of coked catalyst in various proportions with E-cat and MAT evaluation under MST conditions using plant feed stock and MAT yield comparison of coked catalyst with E-cat.

2. Materials and methods

2.1 Feed stocks

Hydro cracker bottom (Unclarified Oil, UCO) from the commercial unit is used for the FCC studies as a feed to the MAT unit. The physico-chemical properties of UCO are given in Table -1. Equilibrium catalyst (E-Cat) and the spent catalyst from FCC unit are used in different proportions as catalyst in MAT unit. The properties of E-Cat are given in Table 2.

2.2 Micro activity testing unit (MAT)

The MAT is a standardized method for determining the characteristics of a particular Fluid Catalytic Catalyst (FCC). This system provides an economical method of comparing feedstock's performance for the same catalyst. The MAT equipment is used to generate possible detailed information on the catalyst selectivity. The catalyst/oil ratio in MAT is adjusted to produce different conversions.

2.3 Design Specification

The design specification of the semi-automatic MAT unit is as follows; Feed injection rate - 0.15 to 0.6 ml/min; Feed injection time - 10,30,50,75 s; Feed syringe temperature - 100°C; Reactor capacity - 4 to 8 gm of catalyst; N_2 flow rate (max) 100cc/min; Air flow rate (max) - 200cc/min; Reaction temperature (max) - 650^0C;Regeneration temperature (max) – 750^oC.

The operating conditions of MAT unit are given in Table 3. Among these operating variables, reaction temperature, C/O ratio and regeneration temperature are taken as commercial FCC unit conditions. The reaction time is the variable that is adjusted to obtain various conversions. It can be extrapolated for constant conversion for comparing various feedstock's. The analyses are carried out in the MAT unit based on the procedure given by Xytel[7]. The product from Mat Unit consists of gases and liquid HC's. The gaseous components are analyzed using Refinery Gas Analyzer and Liquid Product is analyzed using Simulated Distillation Technique (SIM DIST)(ASTM D-2887)

UOP offers reactor catalyst recovery technology, which can increase the throughput of the unit by increasing the cat/oil ratio. The technology involves partially recycling the spent catalyst from reactor stripper to the bottom of the riser and increases the catalyst/oil ratio for the reaction. The other part of the spent catalyst is sent to the regenerator, where the coke on the catalyst is removed. Since only a partial amount of spent catalyst is sent to the regenerator the regeneration capacity can be increased and hence for units with limitations on MAT this could be useful. With this view, a study was carried out in MAT unit for simulating this concept of partial recycling of the spent catalyst from reactor stripper. The various composition of catalyst is one of the important parameter in the yield and selectivity of FCC process. From the physico chemical properties, the E-cat from fluidized cracking unit limits the addition of spent catalyst. The effect of addition of 10%, 30% and 50% E-cat to spent catalyst and the ratio of catalyst to oil are studied using MAT unit with UCO. The yield pattern was compared for various catalyst combination of Ecat + spent catalyst at constant conversion 91.

3. Results and Discussion

The various composition of catalyst is one of the important parameter to be considered for the yield and selectivity of FCC process. The catalysts used in this study were characterized and given Table 2. This project aims at studying the effect of addition of 10%, 30% and 50% spent catalyst and varying ratio of catalyst to oil.

Feed Unclarified oil collected from the commercial unit was characterized and their properties are listed in Table 1. Equilibrium catalyst from the commercial unit Micro Activity test reactor described in the earlier chapter. The typical micro activity test conditions used in the present study are given in Table 3. The reaction was carried out at 535° C with 6 gm of the catalyst. Catalyst to oil ratio different the products obtained in the MAT unit were analyzed by gas chromatography. The results obtained in the MAT various combinations of catalyst are given in Table 4. The corresponding LPG compositions also presented.

The results obtained in the Micro Activity Testing unit for various combinations of catalysts are shown in Fig.1 to Fig.6. Figure 1 indicates the production of light gases for the different combinations of E cat and spent catalyst and C/O ratio. From the figure it is observed that the production of light gases is high for E-cat + 10% spent catalyst mixture and at C/O ratio is 4. From Fig.2 it is observed that the production of LPG is high at C/O ratio 6 and for the E-cat and 50% spent catalyst mixture. The gasoline production is also high at this condition (Fig.3). The formation of diesel and residue are high (Fig.4 and Fig.5) at the C/O ratio of 4 and for the E-cat and 50% spent catalyst mixture. With increase in the spent catalyst composition the diesel production is high, but decreases with increase in C/O ratio. From Fig.6 it is found that the coke formation is high for the E-cat and 30% spent catalyst mixture and at C/O ratio of 4.

The component wise breakup of LPG is shown in the table 4 for various mixtures. From the Table 4 it is observed that the propane and isobutene are more when the C/O ratio is 5. It is also observed that the composition of propylene, isobutylene, Trans 2-Butene, Cis 2-Butene and Butene-I decreases with spent catalyst in the mixture. There is a significant increase in propylene yield when C/O ratio increases. The yield of isobutylene also increases when spent catalyst is procured along with regenerated catalyst.

4. Conclusions

The characteristics of FCC catalyst and spent catalyst are studied. The effect of 10%, 30% and 50% (wt) of E-cat and spent catalyst are studied by using MAT unit with UCO. The yield pattern was compared for various catalyst combination of Ecat + spent catalyst at constant conversion 91. With spent catalyst in the blend the LG yield decreases, with increase in C/O ratio. There is no significant change in bottoms (residue) yield, while there is a decrease in the diesel when C/O ratio is increased from 4.0 to 6.0. There is a significant increase in propylene yield when C/O ratio increases. The yield of isobutylene also increases when spent catalyst is procured along with regenerated catalyst. .

Acknowledgment

The authors wish to express their gratitude for the support extended by the authorities of Tamilnadu Petrochemicals Ltd., Chennai, India in carrying out the research work in their laboratory.

Table 1. Physico- Chemical Characteristics of UCO

UCO	Value
Specific gravity@15/15 ºC,g/cc	0.8462
API gravity	35.7
Kinematic viscosity @ 100ºC,cst	4.88
Pour point, ºC	45
Flash point, ºC	226
RCR,%wt	0.023
Aniline point, ºC	118
Saturates,%wt	97.6
Aromatics,%wt	2.4
Sulfur,%wt	300
Nitrogen,ppm	18
Nickel,ppm	0.03
Vanadium,ppm	0.01

Table 2. Equilibrium Catalyst Properties

Equilibrium Catalyst Properties	Value
Apparent Bulk Density,(g/cc)	0.863
Average particle size,μ	91
PSD-40 μ (wt%)	1
-80 μ (wt%)	33
Surface Area ,m^2/s	167
Pore Volume,(g/cc)	0.22
Na (%wt)	0.5
Ni (ppm)	191
V, (ppm)	100
Fe,(%wt)	0.49

Table 3. Operating Conditions of MAT unit

Reaction Temperature	535° C
Catalyst	E-Cat + Spent cat (10%, 30% & 50%)
Catalyst weight	6gm
Feed weight	1,1.2 and 1.5 gms
C/O Ratio	6,5 and 4
Regeneration Temperature	650° C
Feedstock	UCO

Table 4. LPG Components wise breakup

Components	E cat + Spent cat 10%			E cat + 30% Spent cat			E cat+50%Spent cat			E-cat
	C/O Ratio									
	4	5	6	4	5	6	4	5	6	4
Propane	3.2	3.3	3.1	3.6	3.3	2.9	3.3	3.2	2.9	3.1
Propylene	10.1	11.1	11.5	11.2	10.7	11.6	11.0	11.6	12.7	13.2
N-Butane	1.5	1.6	1.7	1.6	1.6	1.5	1.5	1.5	1.5	1.5
ISo-Butane	9.3	10.2	9.8	9.7	9.9	9.1	8.5	8.4	8.8	8.5
Iso- Butylene	1.9	2.3	2.7	2.3	2.6	2.7	2.2	2.7	3.3	3.1
Butene-I	1.2	1.5	1.8	1.4	1.6	1.7	1.3	1.5	1.9	1.9
Trans 2-Butene	1.3	1.6	2.0	1.4	1.7	1.9	1.4	1.7	2.1	2.0
Cis 2-Butene	0.9	1.2	1.4	1.0	1.2	1.3	1.1	1.2	1.5	1.5

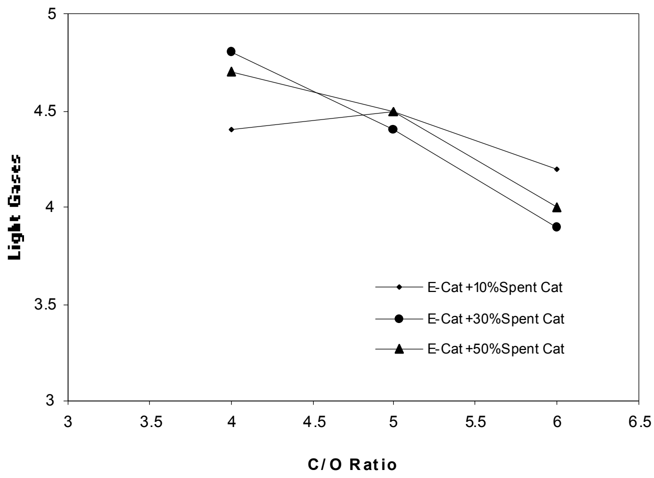

Fig.1. Effect of C/O ratio and Catalyst composition on light gas

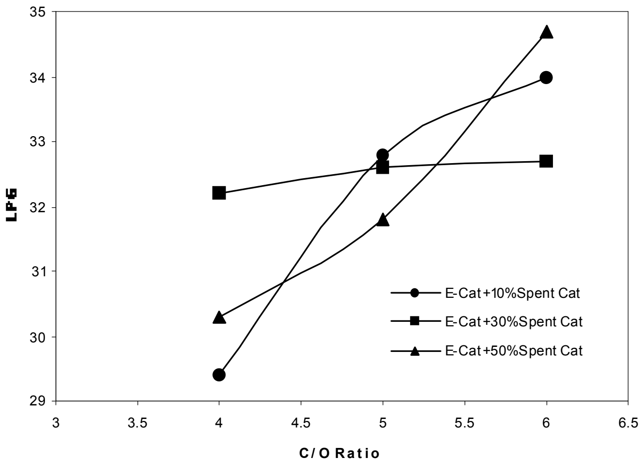

Fig.2. Effect of C/O ratio and Catalyst composition on LPG

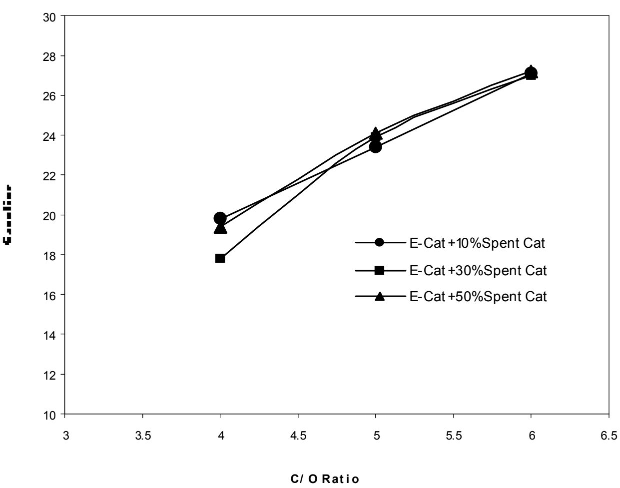

Fig.3. Effect of C/O ratio and Catalyst composition on Gasoline

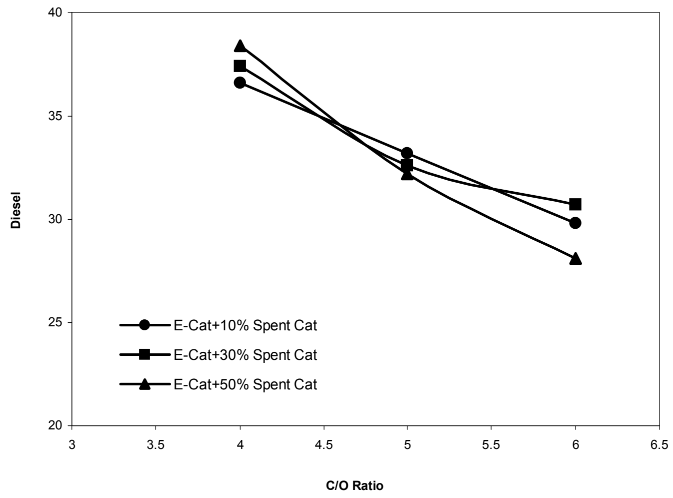

Fig.4. Effect of C/O ratio and Catalyst composition on Diesel

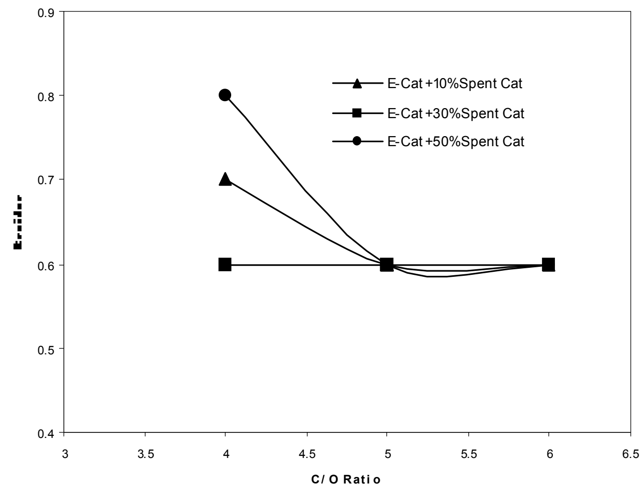

Fig.5. Effect of C/O ratio and Catalyst composition on Residue

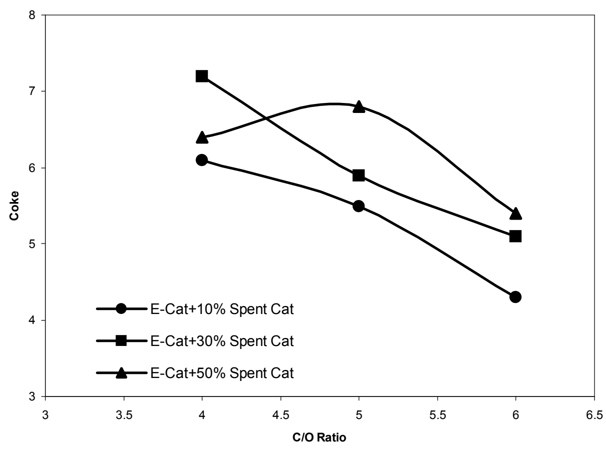

Fig.6. Effect of C/O ratio and Catalyst composition on Coke

References

1. Kunii D. and Levenspiel O., *Fluidization Engineering*, John Wiley & sons, 1969, New York.
2. Lu Y., He M.Y., Shu X.T. and Zong B.N., Exploratory study on upgrading 1-butene using spent FCC catalyst/additive under simulated conditions of FCCU's stripper, Applied Catalysis A: General, 2003, 255, 345-347.
3. Bartholomew C.H., Catalyst deactivation in hydro treating of residua: a review, In catalytic hydroprocessing of petroleum and distillates, Marcel Dekker, Inc., 1994, New York.
4. Jimenez J.M., Trejo S., Pawelec B. and Fierro J.L.G., Regeneration of an industrial Hydro treating Catalyst used for long time on – stream, Symposium of regeneration Reactivation and Reworking of spent catalysts, presented before the division of petroleum chemistry, 1993.
5. Rajasimman M. and Prabhakaran M., Micro simulation studies on coked fluid catalytic cracking catalyst, Paper presented at 60^{th} annual session of Chemical Engineering Congress - 2007 (CHEMCON - 2007), Kolkatta, India.
6. Wallenstein D., Harding R.H., Witzler J. and Zhao X., Rational assessment of FCC catalyst performance by utilization of Micro Activity Testing, Applied catalysis A:General, 1998, 167, 141-155.
7. Zytel, Operating manual for MAT unit, (ZYTEL), CPCL, 1996.

*****