

**STUDY OF PARAMETERS THAT AFFECT THE ISO- PRODUCTS
FORMATION IN FCC UNIT**

A Project report

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ABSTRACT

It has been seen in the refinery that Iso -products have major uses and its production is of utmost importance. So new units have been set up for it that cost too much for the refiner and the cost economy degrades, so the major research which we emphasis here is the production of iso products from FCC unit itself so that the cost of installing new unit is saved. So in this project we tend to find out all the parameters that effect the Iso products formation in the FCC coloumn.

Out of various parameters found out two parameter that can be made change on a catalyst can be the unit cell size and the amount of rare earth as it is shown that increasing both the compound tends to isomerize more and will lead to much more formation of iso products. The other parameters like the effect of hydro treating, the extra frame work alumina, the zeolite effect all other were also been showed so that whenever we tend to form a catalyst, after the reaction modeling these properties should be checked out and thus will lead to a better catalyst formulation.

Then we come to know about how the iso products can be increased in a unit by the Cracking of PAH (Polycyclic Aromatic Hydrocarbon) compounds which crack to give various products and also increases the iso products formation. The problem with these compounds are that generally they do not tend to crack easily in FCC condition so are done in hydro processing units, our aim here is to crack these compounds in the FCC condition itself so that no need of further processing of LCO (Light Cycle Oil) or CLO (Clarified Light oil) is required in hydro processing then we find out the techniques of how to crack these PAH compounds. The reaction modeling was done on to select which component and out of lot of options including the light straight run naphtha, heavy straight run naphtha, light FCC naphtha we tend to choose heavy straight run naphtha for its better capability to undergo cracking due to its long chains as compared to the light straight run naphtha. Now since the HSRN (Heavy straight run Naphtha) is found out we now tend to check the proportion in which the feed should me mixed out so that much more of a aromatic breaking mechanism is supported rather than the way through which the Naptheno Aromatics compounds revert back to form PAH. So for this the predictability of feed is seen in which the amount of aromatics should be high and the naphthenic aromatic compounds should be least, so in this order we ought to know the best feed possible, this is calculated by the K-factor and the N-D-M method and thus by this the overall ratio of mixture is thus obtained.

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NOMENCLATURE

AL	Alumina
ACE	Auto Catalytic Emitted
Ca	% Aromatics
Cr	% Ring Structure
Cp	% Parrafin
CCR	Carbon Conradson Residue
C-C	Carbon-carbon
C-H	Carbon hydrogen
CLO	Clarified Light Oil
C-H	Carbon hydrogen
EFAL	Extra Frame Work Alumina
FAL	Frame Work Alumina
FCC	Fluid Catalytic Cracking
HSRN	Heavy Straight Run Naptha
I	ISO
K	Watson Factor
LCN	Light Coker Naptha
LCO	Light Cycle Oil
LSRN	Straight Run Naptha
MeABP	Mean Average Boiling Point
MON	Motor Octane No
N	Normal
RON	Research Octane No
PAH	Polycyclic Aromatic Hydrocarbon
SI	Silica
S	Sulphur
SG	Specific Gravity
USY	Ultra Stable Y
VABP	Vapour Average Boiling Point
X	Factor

CHAPTER 1 INTRODUCTION

It has been seen in the refinery that iso -products have major uses and its production is of utmost importance. So new units have been set up for it that cost too much for the refiner and the cost Economy degrades, so the major research which we emphasis here is the production of iso products from FCC unit itself so that the cost of installing new unit is saved. So for understanding the FCC process various literature reviews were made on the following topic.

1.1 Basic chemistry of Isomerization in FCC

Fig 1.1 Various Cracking schemes in FCCU

1. Cracking:	
Paraffins cracked to olefins and smaller paraffins	$C_{10}H_{22} \rightarrow C_4H_{10} + C_6H_{12}$
Olefins cracked to smaller olefins	$C_9H_{18} \rightarrow C_4H_8 + C_5H_{10}$
Aromatic side-chain scission	$ArC_{10}H_{21} \rightarrow ArC_5H_9 + C_5H_{12}$
Naphthenes (cycloparaffins) cracked to olefins and smaller ring compounds	$Cyclo-C_{10}H_{20} \rightarrow C_6H_{12} + C_4H_8$
2. Isomerization:	
Olefin bond shift	$1-C_4H_8 \rightarrow trans-2-C_4H_8$
Normal olefin to iso-olefin	$n-C_5H_{10} \rightarrow iso-C_5H_{10}$
Normal paraffin to isoparaffin	$n-C_4H_{10} \rightarrow iso-C_4H_{10}$
Cyclohexane to cyclopentane	$C_6H_{12} + C_5H_9CH_3$

Fig 1.1 explains here are the few reactions that take place in the FCC columns and the condition of them being at the FCC temp and Atmospheric Pressure. Here we can see that Iso products do form from the FCC reactions and the basic reactions are given. There are two type of cracking that occur in the FCC.

1.2 Protolytic Cracking

John Dwyer *et al.*, (2001) explained Cracking occurs at lesser Conversion (needs high Activation energy). At starting the Pryolytic Cracking which involves Protonation produces C-C or C-H bond and a surface Carbenium ion.

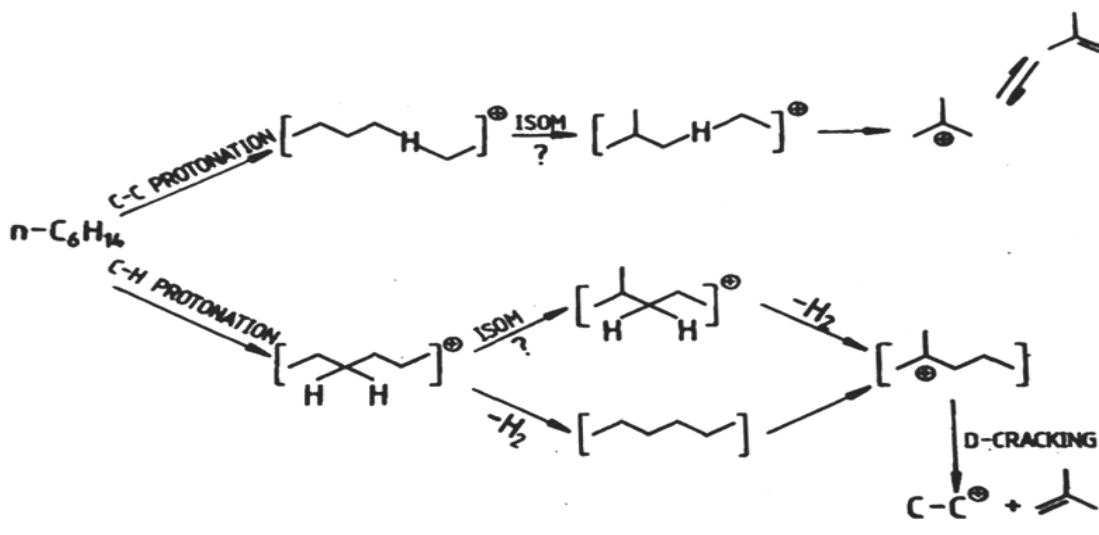
1.3 Carbenium Ion Cracking

This Carbenium ion after that reacts with Alkane or Alkene molecule for further cracking which is Classical cracking.

John Dwyer *et al.*, (2001) explained here we have engaged n-hexane for reactions. It was found out that (Iso Olefin / Iso Paraffin) was in equilibrium because of difficulty of converting n-butyl ion to Iso butyl carbenium ion.

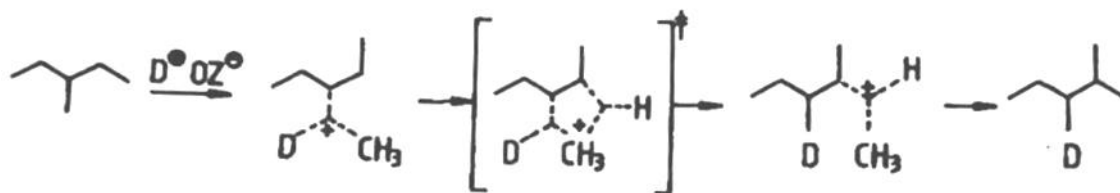
It should not be in equilibrium, but it is .So this increased amount of Iso products are due to cracking of monomer species ($n > 6$). Here we can give an example of this type of Protolytic cracking (Fig 1.3)

Fig 1.3 N-Hexane cracking through different routes



John Dwyer *et al.*, (2001) explained we can see Iso Paraffin formation by protonation from C- C, H-C bond former to Protolytic Cracking. Such reactions are not known in solution but NMR result shows this cracking and Isomerization of Iso-hexene compound.

Fig 1.3 Scheme showing the movement of formed positive Cation



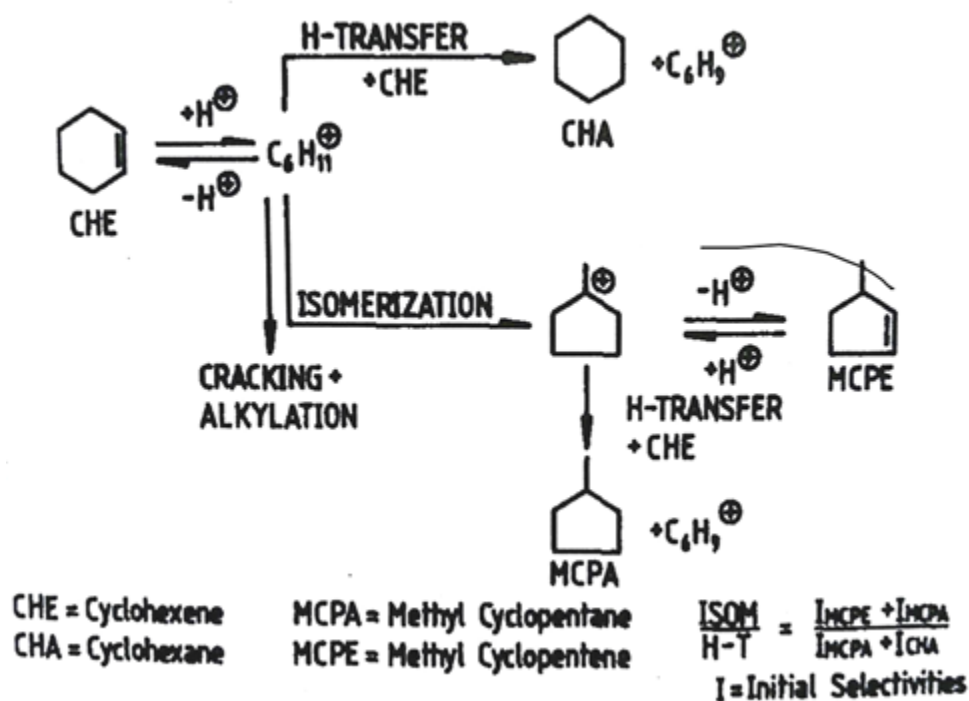
Direct skeletal isomerization of Carbonium ion in zeolite can describe the detected C4 composition but must be observed as highly speculative. At upper conversion, the reaction products are mainly determined by carbenium ion selectivity (Fig 1.4)

CHAPTER 2 SURVEY OF LITERATURE

- 1) Isomerization / Beta scission (monomolecular).
- 2) Alkylation / Oligomerisation / hydrogen transfer (bi –molecular).

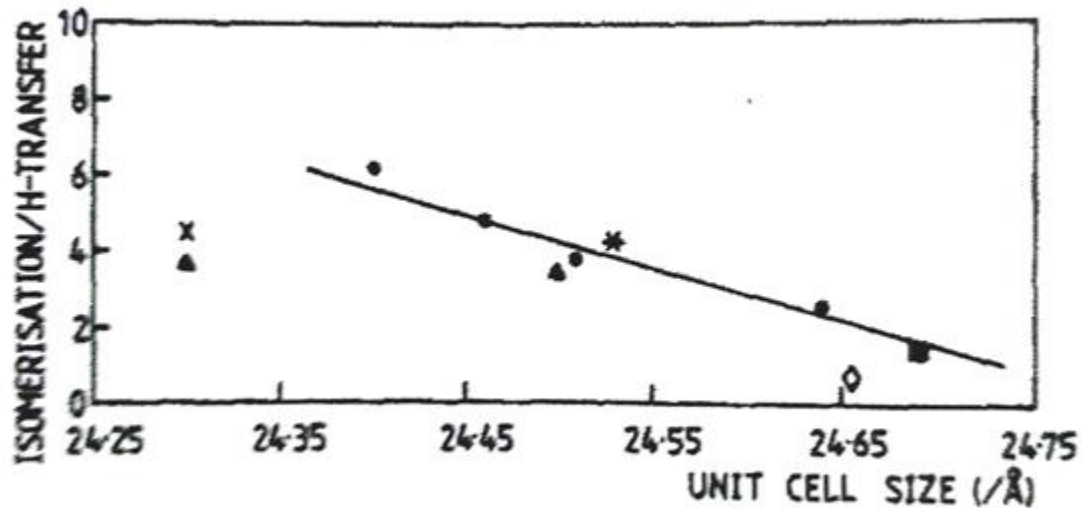
John Dwyer *et al.*, (2001) explained the equilibrium, of single molecular vs. bimolecular is affected by acid site density. The pathway of cyclo hexane provides us with view of influence of site density on rest of the isomerization to hydrogen transfer (see figure 2.1).

Fig 2.1 Cyclo hexane transition to undergo Isomerization.



This gives an idea of that the hydrogen transfer and isomerization reaction can follow whichever path the equilibrium. Now if we compare these reactions in accordance with the Unit Cell Size it will give an fair idea of how these hydrogen transfer and Isomerization reactions go hand in hand and thus we will be able to get an idea of what happens when we increase or decrease the Unit Cell Size.

Fig 2.2 Isomerization vs. Hydrogen transfer



The effects for zeolite Y which composes of different framework composition, diff (Si/Al) ratio, show the ratio (Isomerisation / HT) decrease as UCS upsurge and acid sites become more extensively spread. In broad direct evidence of Carbenium ion in zeolite is limited and are supposed to be very short lived transients (fig 2.2)

John Dwyer *et al.*, (2001) explained we can see here the sites are close, as the H transfer provides it absorption of other reactant molecule.

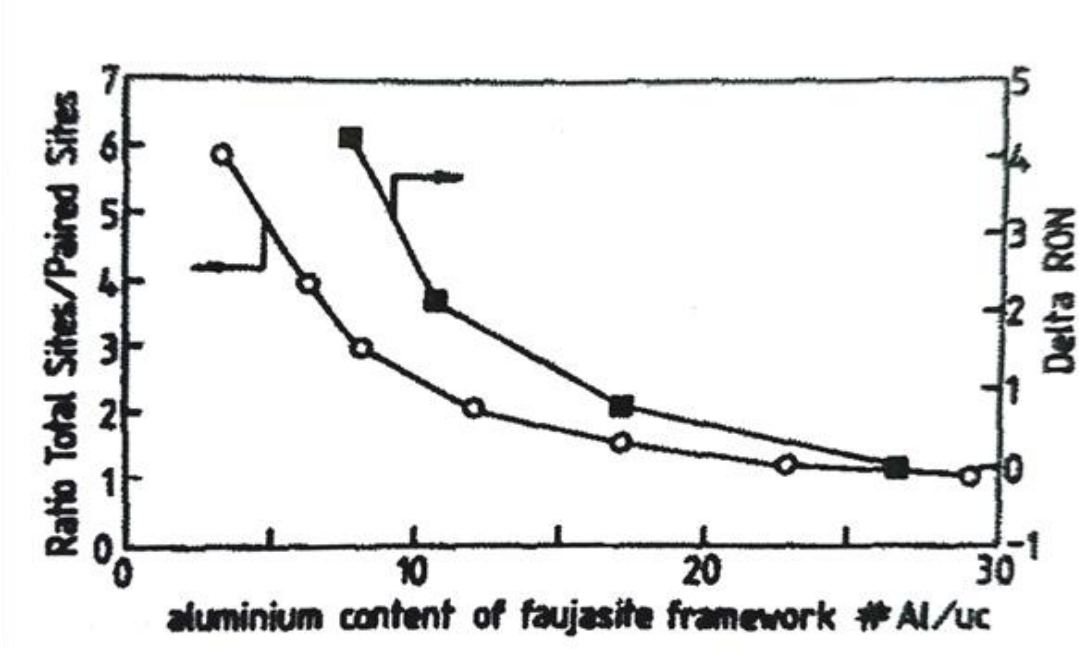
2.1 Effect of acid site

→ John Dwyer *et al.*, (2001) explained The removed EFAL has effect on the ratio between Isomerization and the hydrogen transfer reaction which in general is reduced by steam Calcination.

→ The [(The total amount of acid site) / (total amount of acid site that pair)] belongs to the quantity of isolated single site at particular framework configuration Si/Al ratio, therefore it leads to change in RON.

→ As density of the acid site becomes lesser the ratio upsurges, the two mono molecular process, isomerization & beta scission rise but the bimolecular Hydrogen transfer becomes less and increases the RON.

Fig 2.3 Ratio of Total sites to paired sites



John Dwyer *et al.*, (2001) explained the Al amount of the framework alumina increases there the total amount of sites that are paired to the amount of total acid site will increase. Zeolite (Y) that has similar framework composition will have different distribution of AL, it all depends on how it was prepared, these changes can be done to check product stream by zeolite modification (Fig 2.3).

2.2 parameters that effect Iso-products

- 1) Hydro treating
- 2) Pore size distribution
- 3) Small stable crystals used
- 4) Matrix effect
- 5) Temperature
- 6) Metals on catalyst
- 7) Conversion
- 8) Rare earth component

2.2.1)HYDROTREATING

H.J. Lovnik *et al.*, (1990) explained that a small amount of hydro treating was done in which a minor hydrocracking was been done to the feed that stated out yes there was partial cracking and the products yield thus changed.

- Mild hydro cracking at 400 degree Celsius.
- There was increase in the Iso - paraffin amount produced, constant production of N- paraffin
- The lighter paraffins showed the biggest enhancement of all, Iso C4 by a factor of 1.5.

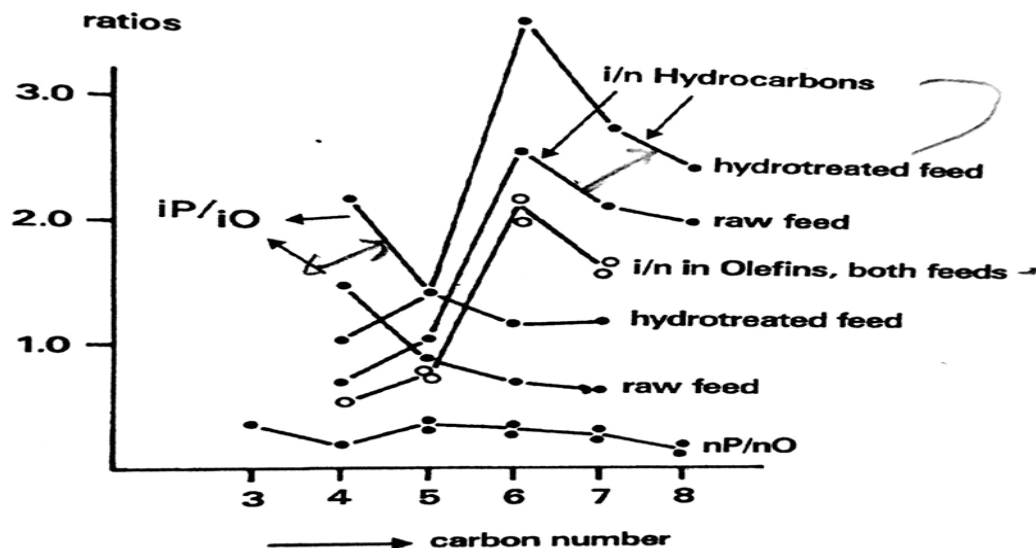
Changes were as follows-

- ic4 = +50%
- ic5 = +41%
- ic6 = +38%
- ic7 = +24%
- ic8 = +28

2.2.2PRODUCT DISTRIBUTION

- Napthenes, open rings in nearly same amount.
- Iso Olefin and normal olefins in nearly same.

Fig 2.4 Iso product distribution in Raw vs. Hydro treated feed



- 1) The figure 2.4 shows that the Iso olefin /n olefin is same in both.
- 2) I/n ratio is higher in hydro treated feed.
- 3) I- paraffin/I olefin is higher in hydro treated feed.

Beside this

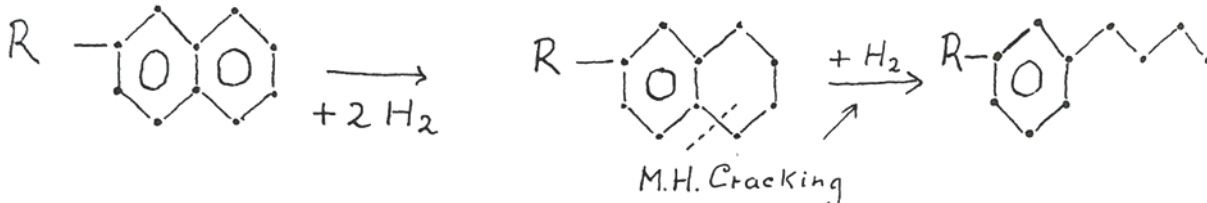
- 1) The Rate of cracking increase by 121 percent.
- 2) Iso-paraffin increase by 51 %.
- 3) Mono ring aromatic increase by 26%.
- 4) The (Iso-paraffin /Is-olefin) ratio increases from 0.90 – 0.50.

Table 2.2.1 Table shows the increased Iso products.

no. of curton atoms	iso- paraff.		normal paraff.		naphtenes		iso- olefins	
	-	+	-	+	-	+	-	+
1	-	-	1.1	1.3	-	-	-	-
2	-	-	1.1	1.0	-	-	-	-
3	-	-	1.4	1.4	-	-	-	-
4	1.80	3.10	0.7	0.7	-	-	1.2	1.4
5	1.74	3.07	0.93	1.00	0.24	0.25	1.94	2.11
6	1.78	3.22	0.40	0.40	0.73	0.91	2.47	2.66
7	1.54	2.62	0.34	0.40	1.01	1.31	2.27	2.11
8	2.31	3.12	0.20	0.20	1.26	1.36	0.55	0.55
9	1.42	1.26	0.16	0.10	0.69	0.65	0.10	0.05
10	0.61	0.55	0.12	0.15	0.16	0.15	0.04	0.05
11	-	-	0.04	0.05	-	-	-	-
Totals	11.20	16.94	6.49	6.70	4.09	4.63	8.57	8.93

H.J. Lovnik *et al.*, (1990) explained the degree of branching is increased for 6-7 c atoms .So we can conclude that hydro treating does increase the amount of Iso paraffins in the feed as well as the aromatic, the aromatics are increased by cracking PAHs which are lesser in octane number (Table 2.1.1).

Fig 2.5 Cracking of a mono ring aromatic via hydrogen addition



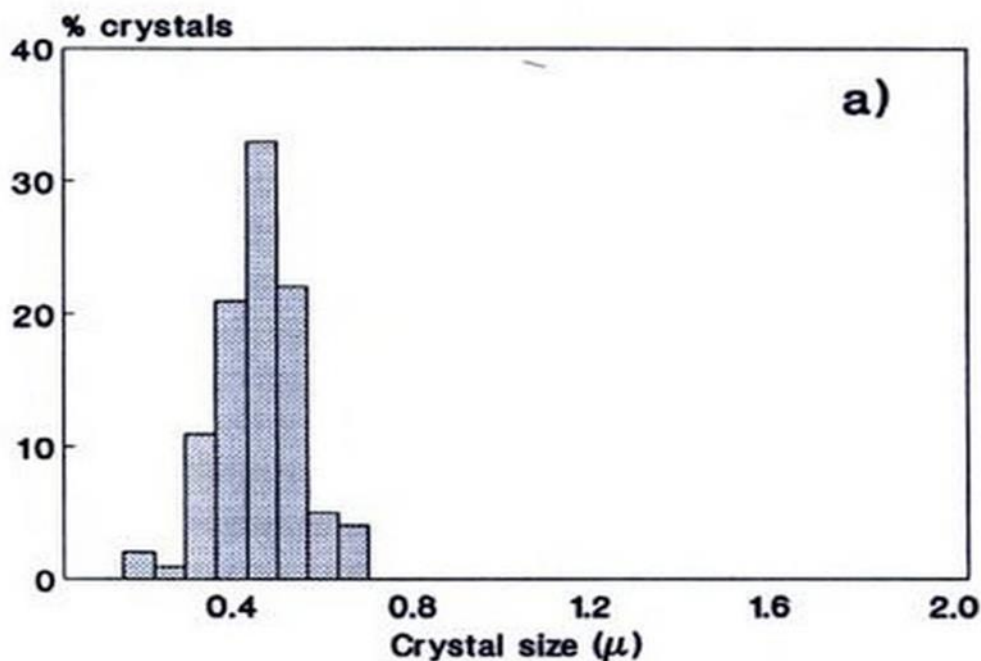
The di ring is cracked by mild hydro cracking and therefore produced mono ring aromatics and these are more in Meta than ortho which increases the OCTANE (Fig 2.5).

2.3 Use of Small Crystallites of Zeolite Y Synthesized with high Si/AL ratio

- 1) Here NAY zeolite was used with Si/AL =3
- 2) Zeolite is HYDROTHERMALLY STABLE and steamed at 750 degree C
- 3) Two NAY Zeolite used
- 4) SK-40 (SI/AL=2.4) (Conventional Y Zeolite)
- 5) IC-1(SI/AL=3)
- 6) Steam Calcined for at 500 degree for 5 hours
- 7) Particle size of NAY =0.59-0.84(After crushing, Pelletizing, Sieving).

H.J. Lovnik *et al.*, (1990) explained these small stable crystallite develop high total conversion, more Iso paraffin, more Iso and n-olefins, than Y zeolite which is conventional, simultaneously produce less n-paraffin though aromatics produced are a bit less but chances to bring aromatics from heavy end is higher.

Fig 2.4 The amount of crystals formed with respect to size



H.J. Lovnik *et al.*, (1990) explained we can see the difference in crystal size of the one where small stable crystals are used is around 0.4 Micron. The results after cracking obtained showed in (Fig 2.4 and table 2.2)

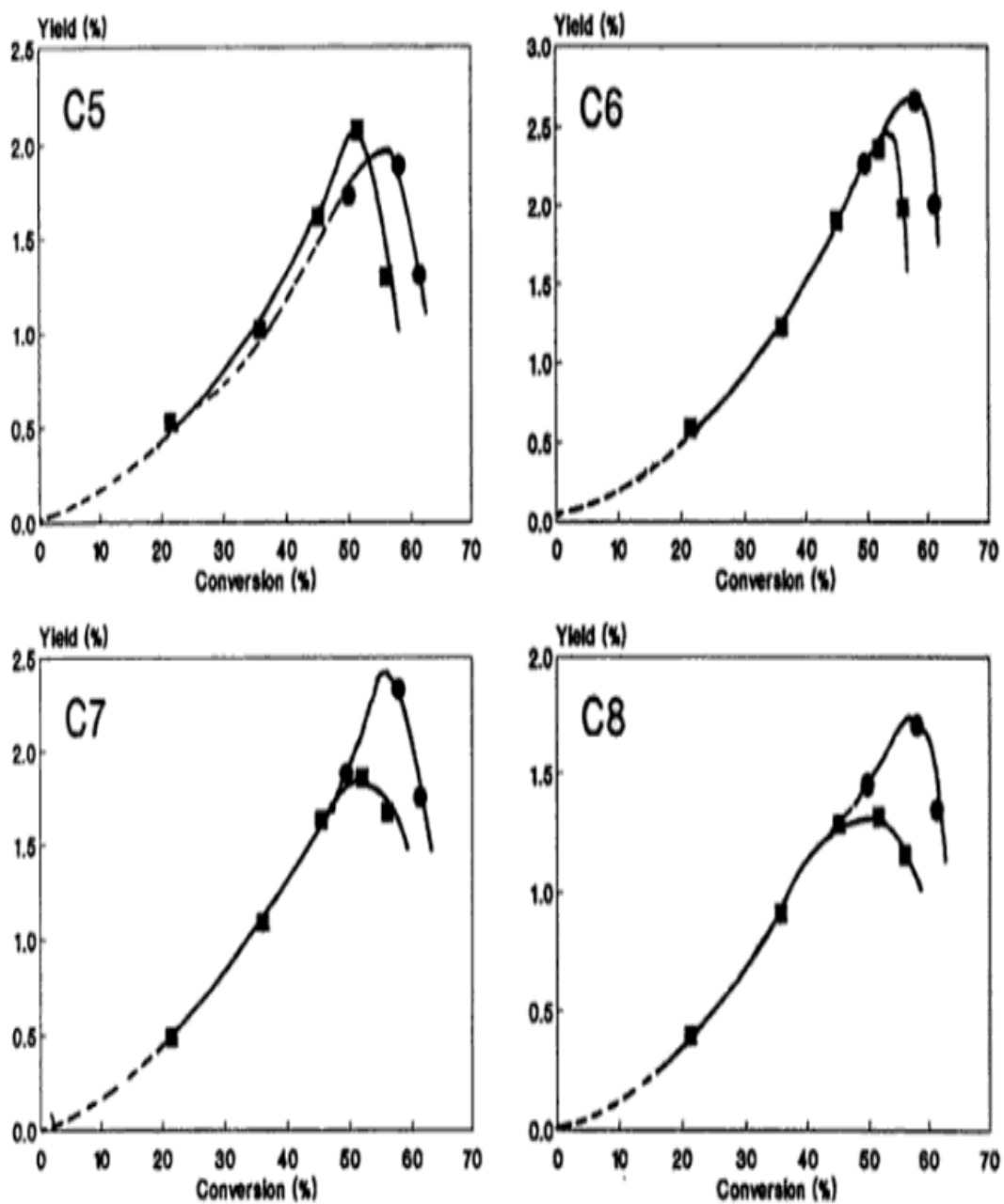
Table 2.2 Stability of various compounds in FCCU

	C5	C6	C7	C8	C9	C10
i-paraffins	(1+2)U	(1+2)U	(1+2)U	(1+2)U*	(1+2)U	(1+2)U
n-paraffins	(1+2)U	(1+2)S	(1+2)S	(1+2)S	(1+2)U	(1+2)U
i-olefins	2U	(1+2)U	(1+2?)U	(1+2?)U	(1+2)U	(1+2)U
n-olefins	(1+2)U	(1+2)U	1U	1U	1U	1U
Sat.Naph.	(1+2)U	(1+2)U	(1+2)U	(1+2)U	(1+2)U	(1+2)U
Uns.Naph.	1U	1U	1U	1U	1U	1U
Aromatic	--	(1+2)S	(1+2)S	(1+2)S	(1+2)S?	(1+2)U

The results after cracking obtained show. I(paraffin/olefin) unstable. Sat / unsaturated Napthene is unstable .

It also shows high selectivity to gasoline and lower coke production, thus it will not only increase RON and MON (Fig 2.5).

Fig.2.5 Yield of various Iso-parrafin which include from C4-C8



Thus from the figure we can see that the amount of these Iso paraffins increased by using small stable crystals, here we can see that from the given paraffins out of all the small stable crystallites have helped us in growing up the Iso-products.

2.4 Main findings of all

These were the two parameters which were searched in detail and found out that Iso products were increased from them and more parameters were found.

→Effect of rare earth

→Effect of unit cell size

→Effect of extra framework alumina

→Effect of carbenium ion selectivity

Takayuki Komatsu *et al.*, (2005) explained as discussed earlier there were parameters that effect the Iso product formation ,the next few parameters that effect the Iso product formation will be given and few of the next parameters that effect the iso products formation.

Takayuki Komatsu *et al.*, (2005) explained we check the effect of framework alumina (FA), the extra framework alumina (EFAL) and Non Frame Work Alumina.

2.5 Effect of Non Frame Work alumina

There was no effect of Non Framework Alumina when an experiment was done with FCC catalyst zeolite and it was found out that there was no change in the Is-product when the non-frame work Alumina per Unit Cell was increased or decreased. So here we can see the effect of Non Framework Alumina which is going to show that how much amount of the effect of loading of Zeolite to Matrix ratio and the effect of non-framework alumina is there if we are going to use it then what effect will it create. The figure that shows it on next page.

Table 2.5 The Effect of Non Frame Work alumina

Zeolite Unit Cell Size, Å	24.26	24.26
Framework Al per Unit Cell	8	8
Non-Framework Al per Unit Cell	27	41*
Conversion, Wt %	74.7	76.2
Gasoline Selectivity (Yield/Conv.)	0.74	0.75
Gasoline Composition, Wt %		
Paraffins	42.7	40.2
Olefins	13.1	13.8
Naphthenes	13.5	13.9
Aromatics	30.6	32.0
C₅ Paraffins	Equil. @ 981°F	
n-Pentane	.40	.09
2-Methylbutane	.54	.91
2,2 – Dimethylpropane	.06	–

2.6 Effect of Matrix activity

Takayuki Komatsu *et al.*, (2005) explained

- 1) High activity to alter gasoline composition tending towards olefins.
- 2) At low matrix/zeolite level or high zeolite/matrix surface area ratio
- 3) N paraffin increase in amount (Table 2.5).
- 4) Iso paraffin increase in amount
- 5) Olefins decrease very seriously
- 6) Napthene ,no change is there
- 7) Aromatics increase in amount
- 8) RON decrease
- 9) MON increase
- 10) Problem is as zeolite content increase the stability decreases
- 11) As matrix content increases the stability (hydrothermal) increases
- 12) Zeolite content (0.75-1.74) % increases the stability decrease (0.5-1.1)%

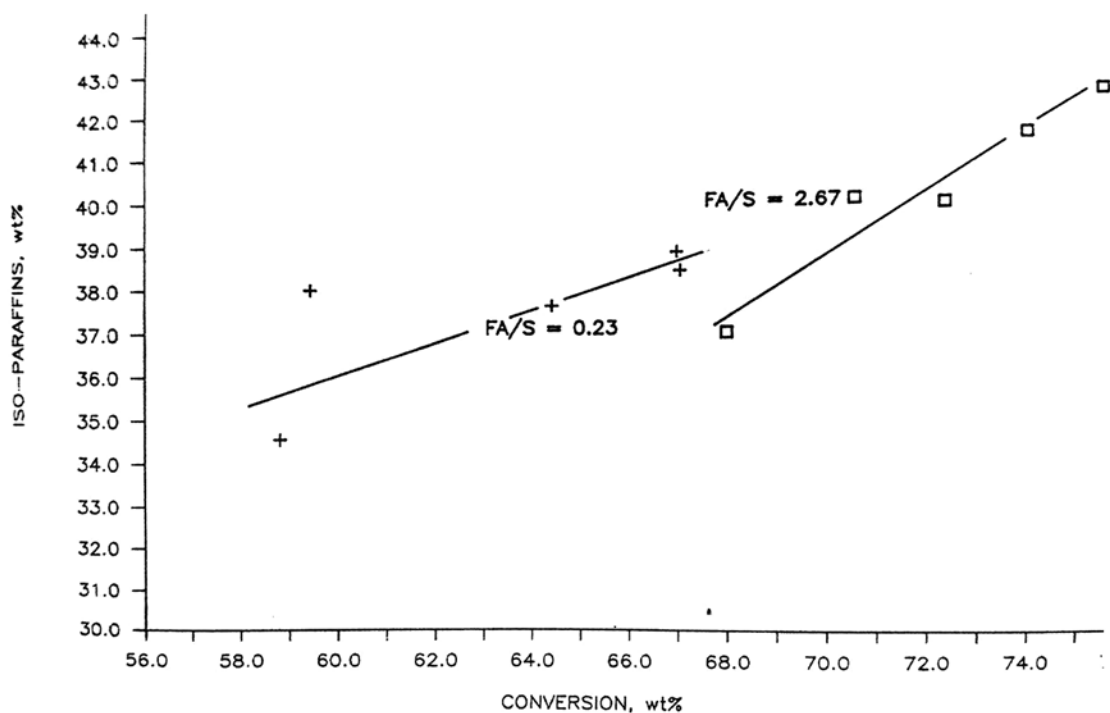
Table 2.6. Effect of Catalyst Matrix activity

	Low Matrix	High Matrix
Zeolite/Matrix Surface Area Ratio	5.2	0.2
Zeolite Unit Cell Size, Å	24.46	24.46
Gasoline Octane Number- RON	94.8	95.5
- MON	82.1	81.3
Sensitivity (RON - MON)	12.7	14.2
Gasoline Composition, Wt%		
n-Paraffins	3	2
i-Paraffins	21	14
Olefins	33	45
Naphthenes	10	10
Aromatics	33	29

An another experiment was done using pseudo bohemite alumina, the parameters and the experiment was done. Lovnik H.J. *et al.*, (1990) explained PSEUDO BOHEMITE AL is used in this case named FA (Table 2.6).

- 1) When high surface area silica binders are used, the ratio of matrix Si /FA can be varied.
- 2) Thus FCC matrix with different active matrix composition but equal.
- 3) Total surface area.
- 4) Equal zeolite surface area.
- 5) Equal total matrix surface area, can be produced.
- 6) Five series of catalyst used for this study with three different active matrix compositions.
- 7) The catalyst surface areas (Total, zeolite and matrix) were held constant for each.
- 8) Different zeolite level were used to test, and at each zeolite level FA/SI was varied.

Fig 2.6 Effect of bonhomie Alumina to Silica ratio



We can see the framework alumina when used at higher rate the slope for iso products is higher and thus the iso paraffins will be formed more FAL will be used greater in amount (Fig 2.6).

2.7 Carbenium Ion Selectivity (Effect of extra framework Alumina)

The carbenium ion cracking, which is an acidic type of Cracking (ionic), has a tertiary carbenium ion that gives branched products. Protolytic cracking with penta coordinated carbonium ion intermediate produce product such as fuel gas..

Takayuki Komatsu *et al.*, (2005) explained now if checked carbenium ion selectivity for the Y type fauzasite. Here we have used ic4 carbenium ion selectivity i.e. that optimum (FAL) or (EFAL) is thus needed to show optimum activity. Stabilisation the EFAL will move to surface upbringing a, aluminum rich surface, that has poor selectivity. This phenomena is counteracted by chemical de alumination (diffusion limited), less alumina depleted surface formed. The cracking activity and selectivity of USY Zeolites are highest when zeolite EFAL is highest, this to be explained in sense of AL depleted surface, formed during chemical process.

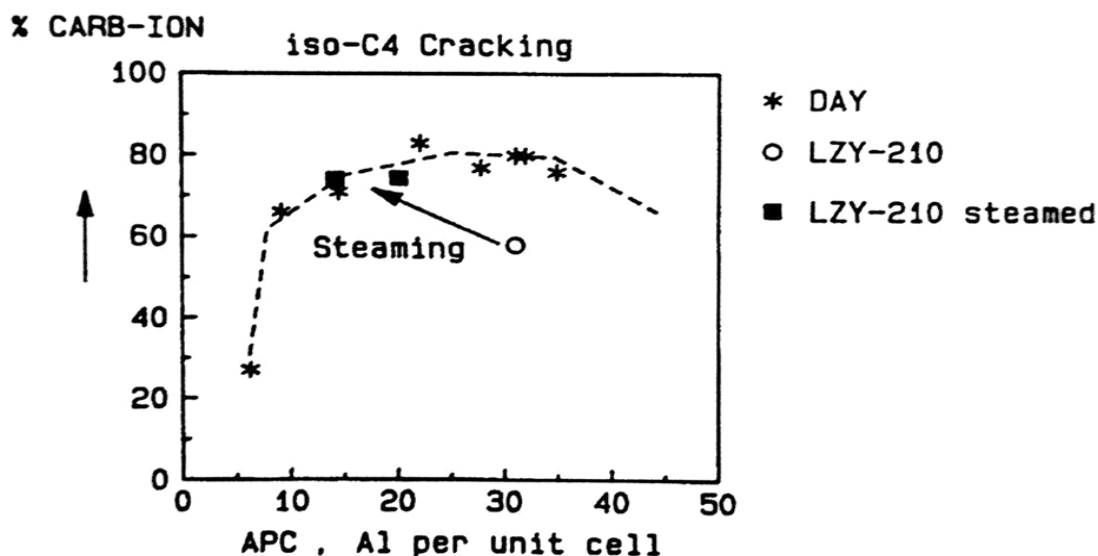
Here we can see the effect of EFAL the branching increases as compared to the traditional zeolites (Fig 2.7).

Fig 2.7 Effect of extra frame work alumina showing the improved distribution by EFAL.

ZELOITE TYPE	Conv. %wt	Gsln %wt	FGAS %wt	C ₂ -iC ₄	iC ₆ nC ₆ DOB
STANDARD REY-USY					
Hydrothermal Stabilization.					
REY					
15% RE ₂ O ₃ on Y	66.4	46.0	2.03	0.63	6.40
REUSY					
5% RE ₂ O ₃ on Y	65.00	43.0	2.15	0.77	5.70
REUSY					
4% RE ₂ O ₃ on Y	65.6	44.2	2.38	0.90	5.25
USY					
1% RE ₂ O ₃ on Y	65.4	42.6	2.36	0.84	5.13
ADZ					
Improved (E)FAL type and distribution.					
RE-ADZ					
4% RE ₂ O ₃ on Y	65.6	44.7	2.02	0.68	6.47
RE-ADZ					
12% RE ₂ O ₃ on Y	66.2	47.3	1.79	0.56	7.02

As the alumina per unit cell increases we can see that the carbenium ion selectivity increases and thus we are bound to get a better improved result in this case.

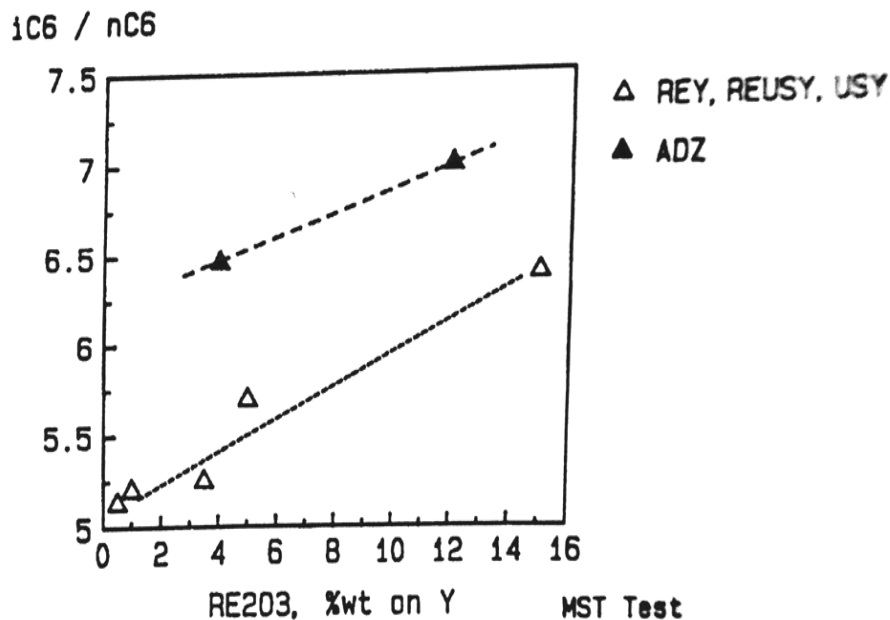
Fig 2.8 The Carbenium ion Selectivity wrt to the Alumina Per Cell



S. Al Khattaf *et al.*, (2003) explained the AL content of the zeolite tends to have effect on polarity of molecular sieve and thus on resulting concentration of hydrocarbons, so i.e. determines the extent of bimolecular reaction. (Fig 2.8, 2.9)

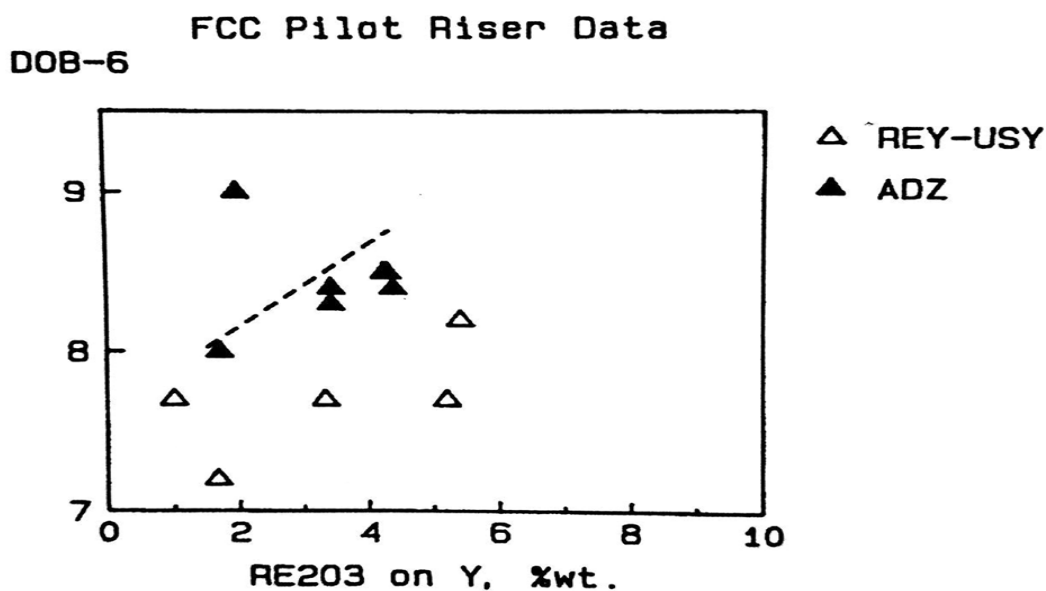
Y zeolite which is made by the ADZ route, has higher branching and (ic6/nc6), than the catalyst by REY or USY route. Here the LZY defines the different type of catalyst which incorporates zeolites and framework ALUMINA.

Fig 2.9 Zeolite type effect on degree of branching



Takayuki Komatsu *et al.*, (2005) explained we see that a higher rate of hydrogen transfer is good for branched product formation. The ADZ route, novel catalyst possesses more selectivity towards carbenium ions. The aromaticity degree and hydrogen transfer would enhance with greater selectivity to carbenium ion (ADZ). The paraffin + paraffinic naphthenes in FCC gasoline reduces by this carbenium ion selectivity.

Fig 2.10 Effect of ADZ



(P+PN) octane depressors thus reduced. Thus as carbenium ion selectivity increased we can increase the hydrogen transfer reaction which is essential for formation of Iso paraffin and aromatics without increasing the octane depressors (P+PN). Less amount of P+PN.

The given figure (2.10) shows out

- 1) REY is converting less.
- 2) ADZ shows linear trending curve.

So for this case we tend to know that this is the much better approach to take rather than to go down with the normal approach of the conventional zeolite which would not produce similar results at all going through it.

2.8 EFFECT OF RARE EARTH

→ ACE Test done on three catalyst at 530 degree centigrade (C/O = 5).

→ RISER Test (C/O = 6).

→ The properties of test are given.

Fig 2.11 Three different Zeolites undergoing changes in UCS due to Rare Earth addition

Item	Re ₂ O ₃ , m%	C/C ₀ , m%	UCS, Å	Collapse temperature, °C	Crystallinity retention, %
USY1	1.8	64	24.52	1,030	74
USY2	8.1	52	24.63	1,004	61
USY3	12.8	53	24.67	1,014	65

Takayuki Komatsu *et al.*, (2005) explained we can see the amount of Rare Earth used are different while the unit cell size is same for both the cases (Fig 2.11)

- 1) Properties and characteristic of these zeolites.
- 2) Number of total acidic sites and the ones strong were more on USY 3.
- 3) Medium strong sites were more on USY 1 and USY 3.
- 4) Yield of branched (Paraffin / Aromatics) more in the zeolite USY 3.
- 5) Ted the olefin production is low in USY 3.
- 6) In USY 3 possesses low acid density so high olefins being produced.
- 7) USY 1 has less hydrogen transfer reaction of olefins which decreases.

After the experiment the following results were found out.

Table 2.8 ACE MAT results through different catalysts at FCC condition.

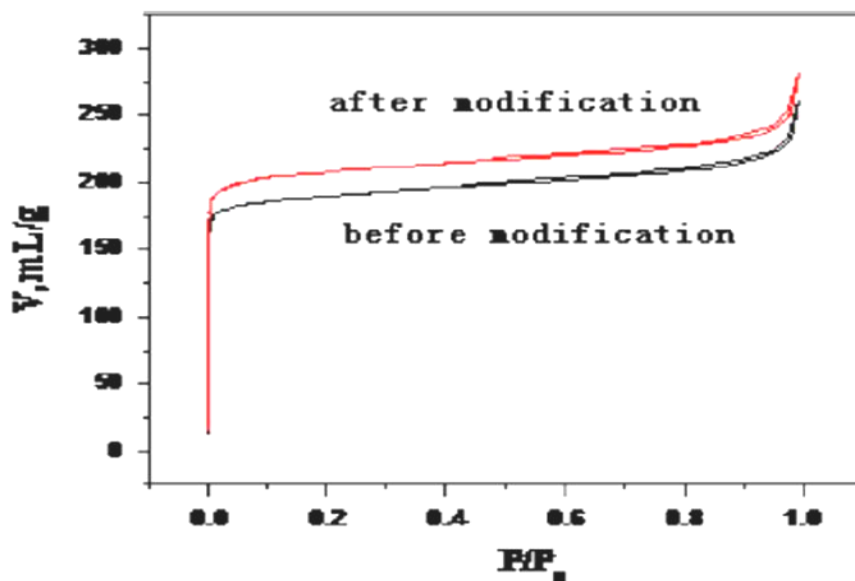
Item	Cat-1	Cat-2	Cat-3
Zeolite	USY1	USY2	USY3
Yield, m%			
Dry gas	2.67	2.55	2.80
LPG	16.84	20.61	22.54
Gasoline	46.54	53.85	54.12
Diesel	15.58	12.45	10.58
Heavy oil	13.03	4.94	3.75
Coke	5.33	5.60	6.20
Conversion, m%	71.39	82.61	85.67
Total yields, m%	78.96	86.91	87.24
Light oil yields, m%	62.12	66.30	64.70
Properties of gasoline			
N-paraffins, v%	6.37	5.31	4.98
Iso-paraffins, v%	14.19	24.19	26.59
Olefins, v%	42.14	26.29	19.90
Naphthenes, v%	4.72	5.04	5.39
Aromatics, v%	32.58	39.16	43.15

We can see the Iso product in Cat-3 has increased which uses rare earth.

2.8.1 Pore structure and cleaning

S. Al Khattaf *et al.*, (2006) explained generally Al or Si fragments were created and they mildly blocked the pores when catalyst was prepared, this made partial deactivation and over cracking of hydrocarbons.

Fig 2.12 Effect of phosphorous modification on pore volume



When high rare earth used it tends convert heavy oil to FCC gasoline with low olefin and

high aromatics, its (total acidic sites + strong site) and high surface area would be producing high cracking ability. MON tends to increase by 0.5 unit RON increase by 0.4 unit, Clean pores allowed fast diffusion of high Octane component before over Cracking (Fig 2.12).

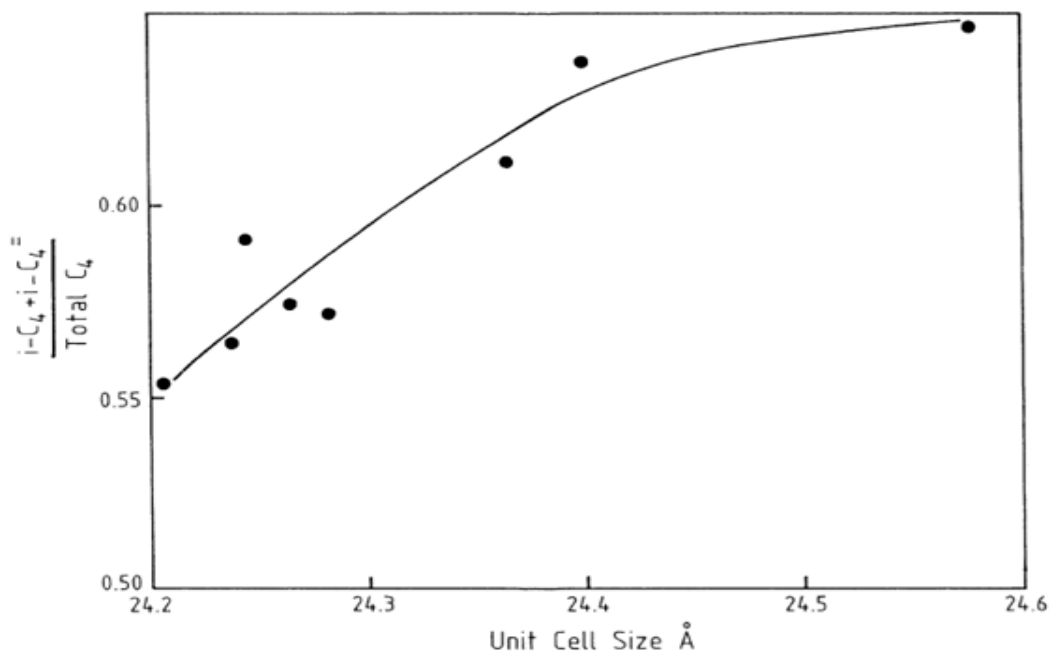
2.8.2 Iso-Effect

Iso-paraffin and aromatics increase due to high cracking ability of Cat-3 (converts PAHS in heavy oil to Aromatics and Iso Paraffins which compensated loss of Octane due to decrease of olefins).

2.9 Chemistry of Rare Earth and Unit Cell Size effect on Iso Products

S. Al Khattaf et al., (2006) as we increase the UCS, the olefins begins decreasing, including the iso-olefins while the amount of iso paraffin increase, and if total parameter is seen here we can see that the iso olefins are getting decreased to produce Iso paraffin, but the rise in iso paraffin is prominent (Fig 2.13).

Fig 2.13 Yield as a function of UCS



Decrease in Iso olefin that becomes constant after some time. Mainly to see the isomerization reaction

The increase of pore size from 24.2-24.4 angstrom. As size increased the effect of it become less. ZEOLITES with high UCS, possess more amount of active sites meaning more n-butyl carbenium ions can be formed. As large energy required, isomerization reaction is more energetically favored followed by desorption or hydrogen transfer rather than cracking.

2.9.1 Interrelation of UCS And Rare Earth

Takayuki Komatsu *et al.*, (2005) explained UCS is directly proportional to AL SITE density (i.e. active site density). More is the UCS, larger is the site density. As catalyst gets aged up in regenerator, UCS reduces by dealumination of zeolite (active sites react with steam and become consumed). So rare earth retards this activity hence maintaining the UCS and acid site prevention. So as the amount of rare earth increases it helps in maintaining the equilibrium state of UCS (zeolite activity site density increase as compared to low RE, so the catalytic activity increase). So activity of catalyst is controlled by both zeolite content and rare earth.

The site density controls both intrinsic activity and selectivity of the zeolite. For HIGH DENSITY ZEOLITES, (High intrinsic activity, Poor coke selectivity, less olefins). Just opposite for LOW DENSITY SITES. So with high UCS we have problem of coke, which can be countered by using VANADIUM traps of Rare earth. A sweet spot of 24.3 was found good to be in line for coke and yield of gasoline.

Rare earth also increases rate of secondary reactions (Hydrogen transfer rxns in this case). Napthene + olefins + aromatic +paraffin if Hydrogen transfer increase, the amount of olefins will be decreased (MON increase). Rare earth provides excellent hydrothermal stability .Upto 1300 degree Fahrenheit for X. Upto 1400 degree Fahrenheit for Overall high activity and stability. UCS decrease during equilibration in regenerator Steam in regenerator removes Aluminum (active acidic AL) form zeolite. RE inhibits extraction of zeolite from its surface, which in turn increases the UCS (equilibrium), it does not increase but just maintain, and the rate of secondary reaction (hydrogen transfer increases).

2.10 How these hydrogen transfer reactions do and their effect

They help in converting PAHs to lighter product, it suggested that 3 ring PAHs can be decomposed to mono aromatic groups, while the 2 was not so reactive, while the work of rare earth is to maintain the rate for hydrogen transfer reactions.

2.10.1 Conversion of PAHs to MONO RING AROMATICS

SOME BASIC CONCEPTS

PAHs not converted to lighter fraction due to difficulty associated with activating aromatic ring in FCCU. Our basic aim here is to show that these PAHs can be converted without applying pressurized H₂ environment. Here two variables are shown.

- 1) Hydrogen transfer (converts 3 ring PAH to mono PAH).
- 2) Rare Earth (not much effect on conversion due to change in loading ,but maintaining hydrogen transfer activity)

Quest – why is it not converted in FCC?

Hydrogenation of naphthalene is more favored in FCC at equilibrium.

2.10.2 Breaking down of PAHs

We see here conversion of three,

- 1) 1-Methyl Naphthalene (1-Mn) 2 ring.
- 2) 9-Methyl Anthracene (9-Mn) 3 ring.
- 3) N-Hexa decane , (n-HD) paraffin.

Given at 516 degree Celcius.

- 1) C/O = (2-4)
- 2) GC analysis was done
- 3) PAH conversion results reduced to 24.29
- 4) Conversion of all 3 increase as C/O ratio increased
- 5) N-hd conversion different in both cases means PAHs and n-HDs interact.

Table 2.6 The conversion of all model compounds and mixtures

Conversion data for the 1-MN/*n*-HD mixture and the 9-MA/*n*-HD mixture over the FCC catalyst with high RE loading.

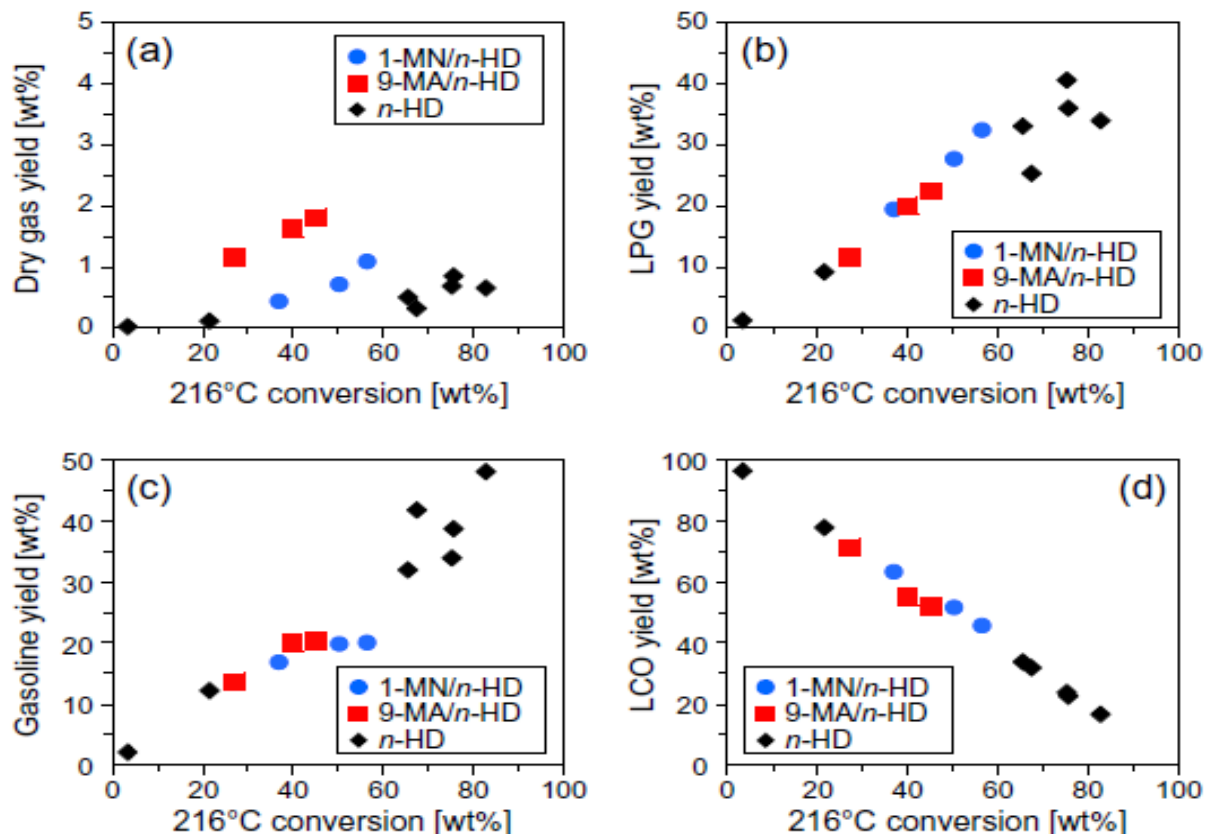
Feed	1-MN/ <i>n</i> -HD			9-MA/ <i>n</i> -HD		
Cat/oil ratio (g/g)	2.0	3.0	4.0	2.1	3.0	4.0
Cat/ <i>n</i> -HD ratio (g/g)	2.3	3.5	4.7	2.5	3.7	4.9
<i>n</i> -HD conversion (%)	43.8	59.2	66.3	30.9	46.2	52.3
1-MN conversion (%)	75.3	77.9	79.8	-	-	-
9-MA conversion (%)	-	-	-	96.4	99.2	99.6
216 °C conversion (wt%)	37.2	50.5	56.7	27.2	40.0	45.0

→3 ring polymerize and form coke

→2 ring remain stable during

→LCO Is decreased and converted to dry gas , LPG , gasoline , coke (Table 2.6, Fig 2.14).


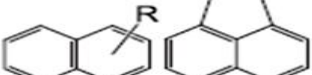
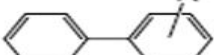


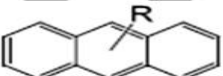
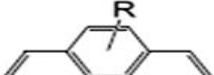
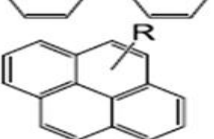
Fig 2.14 The yield of model compounds to various products of FCC



Iori Shimada *et al.*, (2015) explained 9 MN/n-HD showed higher coke yield showed higher coke yield than n- HD, while 1-MN to n-HD showed little effect i.e. 3ring PAH tend to polymerize and form coke while 2 PAH are stable. Many aromatic along with naphthene were found in product. Some of these rings were produced by cyclization other by hydrogenation reaction of PAHs. Iori Shimada *et al.*, (2015) explained .It is known hat sat rings of naphthenes can be cracked by beta – scission mechanism during cat cracking. Here the cracking of polycyclic compounds is mainly due to hydrogenation combined together with beta scission. So this acceleration of reaction pathway will thus contribute in PAH s cracking without necessity of pressurized hydrogen atmosphere. The results produced were (Fig 2.15).

Fig 2.15 The various PAH compounds found in Heavy crude in FCCU

Classification of aromatic products (R represents an alkyl group).

Number of aromatic rings	Components	Examples of molecular structure
Monocyclic aromatic hydrocarbons	Alkylbenzene	
2-ring aromatic hydrocarbons	Alkyl naphthalene	
	Biphenyl	
	Dihydroanthracene	
	Dihydrophenanthrene	
3-ring aromatic hydrocarbons	Alkylanthracene	
	Alkylphenanthrene	
4-ring aromatic hydrocarbons	Alkylpyrene	

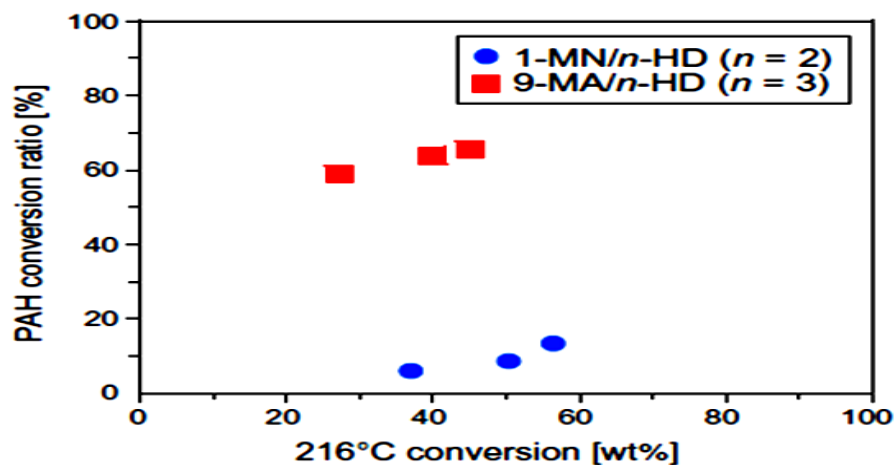
Result

→ 3 ring PAH Conversion > 60 %.

→ 2 ring around 10%

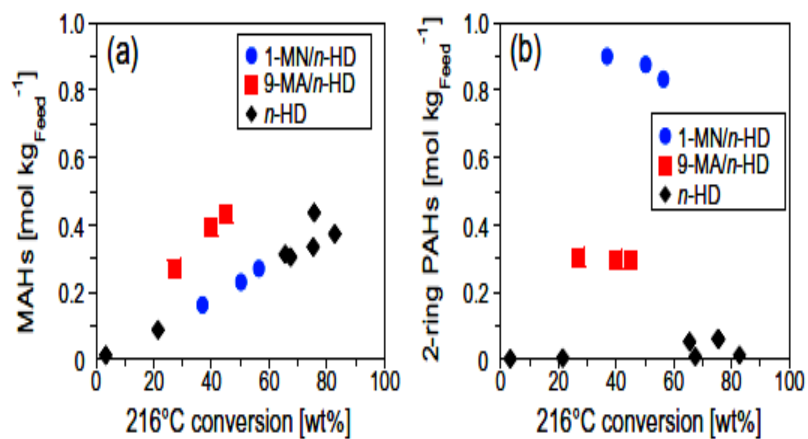
→ 3 ring more reactive than 2 during cat cracking on FCC catalyst

Fig 2.16 Conversion of 2 ring PAH compounds of the given model compounds.



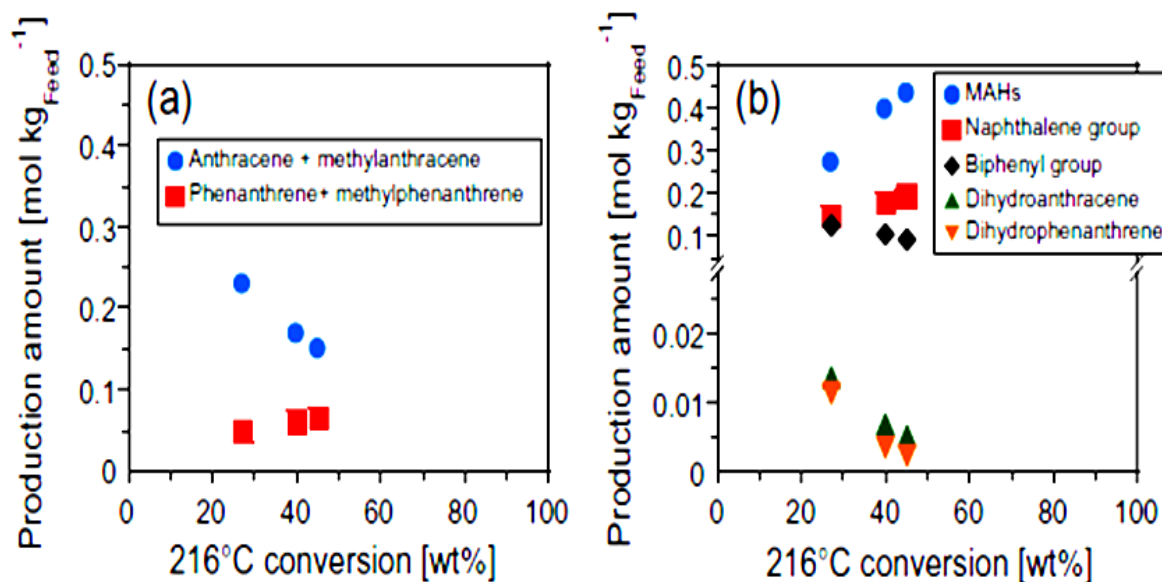
Iori Shimada *et al.*, (2015) explained three ring have greater affinity to convert to MAHs. 2 ring converts to MAH, 2 ring MAH, Coke (all go in parallel). Thus to increase gasoline yield conversion should be accelerated (Fig 2.16).

Fig 2.17 Amount of MAH and PAH in the catalytic conversion



Iori Shimada *et al.*, (2015) explained As conversion increase, Anthracene decrease, Phenanthrene increase (later is more stable and this suggest rapid isomerization of 3 ring PAH).

Fig 2.18 Production of various groups and molecules after catalytic conversion.



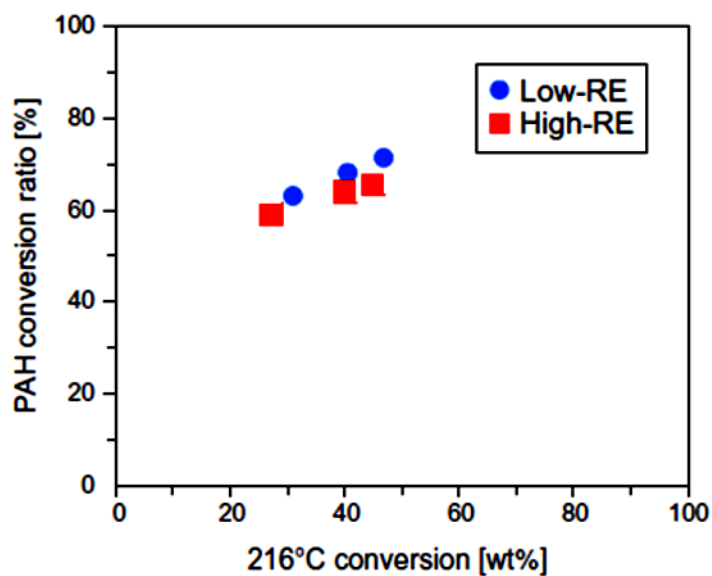
Bi phenyl compound, Di Anthracene etc. decomposed by further reaction (i.e. they were reaction intermediates). Low amount of these compounds (Fig 2.18).

2.10.3 Effect of rare earth loading

9 MA/n-HD mixture analyzed over different rare earth loading. Sufficient steam deactivation done to exhibit same hydrogen transfer. So by this we eliminate hydrogen transfer effect and check rare earth effect on cracking catalyst. Both of these high and low RE earth loading now have comparable UCS. Equal UCS so comparable hydrogen transfer activity. Iori Shimada *et al.*, (2015) explained figure shows that that with less RE coke yield increase, rest all (LPG, dry gas, gasoline, LCO) yield are same i.e. RE has little effect on yield of cracking catalyst. Then we checked hydrogen transfer activity which was same. (Butene /butane) ratio, Olefinicity decreases with increasing hydrogen transfer).

So rare earth here we can say that does not affect the cracking but it helps in stabilizing the catalyst and thus used.

Fig 2.17 Conversion of MAH on a mixture of 9 MA at different Rare earth loading.

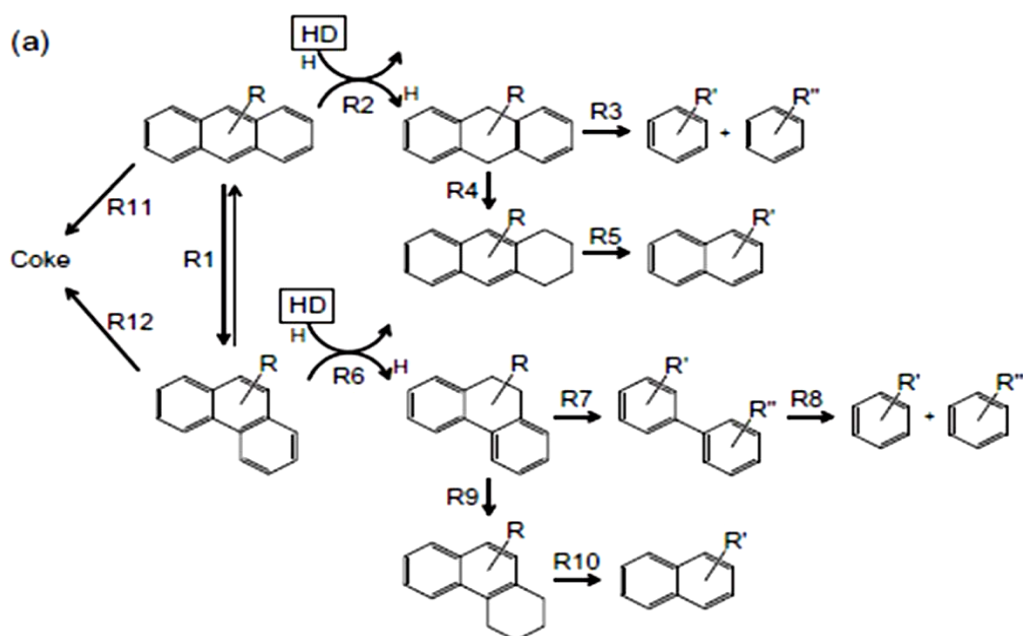


So rare earth can be attributed to simply by maintaining the hydrogen transfer activity of USY zeolite by stabilizing the catalyst against steam deactivation (Fig 2.17).

2.10.4) REACTION MECHANISM

.Hydrogen transfer makes significant contribution to 3 ring PAH. Conversion of 3 ring PAH proceeds by Bi Phenyl, Di Hydro Anthracene, Di Hydro Phenathrene and generates Alkyl benzene and Napthalene. Isomeration of 3 ring PAH proceeds very quickly.

Fig 2.18 Different reaction model scheme for PAH conversion.



1) Isomerization of 3 ring PAHS (R1 and R2)

The reaction starts with Initiated by hydrogenation of aromatics ring by hydrogen transfer reaction and then forms the dehydrogenated Aromatics. Iori Shimada *et al.*, (2015) explained the 1st intermediate is in a sense supposed to be hydrogenated at (9,10) position as this position has comparatively higher than (1,2,3,4) position of anthracene and phenanthrene. Also less amount of hydrogen req to hydrogenate center ring than outer ring (Fig 2.18).

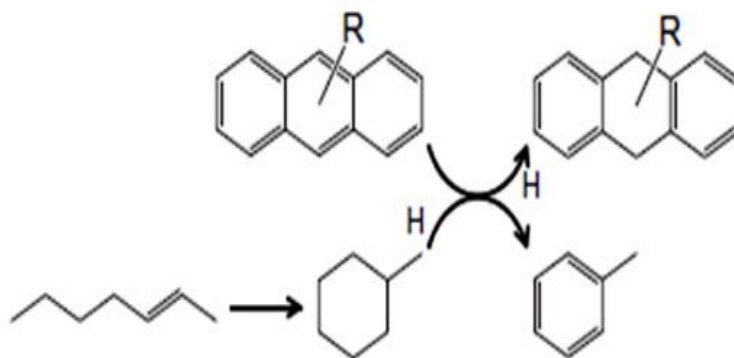
2) Beta scission reaction (R3, R7, R8)

Cracking of di hydro phenaphthrene occurs via the bi-phenyls that were observed as intermediates.

3) Rest of the reactions

After that these formed Aromatics are tend to isomerize down and after that hydrogenate to tetra hydrogenated Aromatics (R4,R9) .Then the decomposition to 2 ring aromatics takes place. These 2 ring aromatics are quiet stable and undergo little decomposition.

Fig 2.19 Transformation of olefin to produce hydrogen compound



Among all steps hydrogen transfer of aromatic ring may be the rate controlling step and is most important in heavy oil cracking. 3 ring PAHs can be converted by hydrogen transfer reaction (Fig 2.19).

2.11) Effect of pore size distribution

The pore size distribution curve gives an idea of the molecular selectivity. If the size of the molecule is within the range then only it will be able to enter the pore, do reaction and come out. Plus it also gives an idea about how those molecules will be distributed and how much pore volume they will obtain. The volume multiplied by area will give the effectiveness of the type of zeolite for particular molecule. Here in this case various iso paraffin molecules are being arranged and we see them in next table and figure.

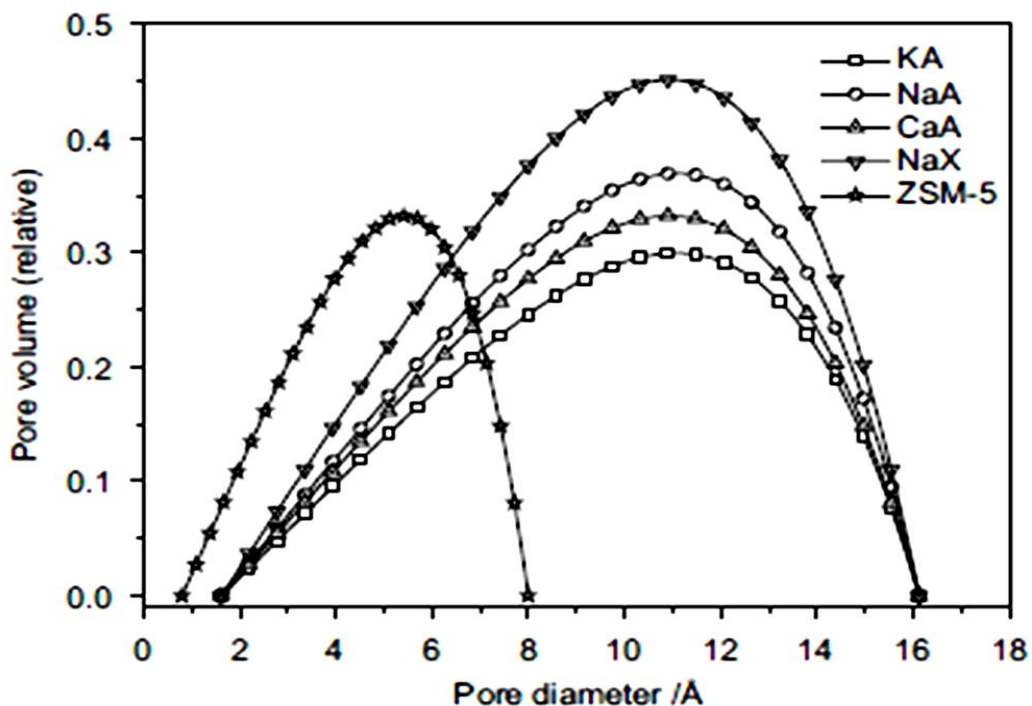
Table 2.6 Pore size data for various Iso-products in range of FCC

Critical molecular parameters for the paraffins, in Å and Å³

Name	Entry	Length	Height	Width	CPK molecular volume	w-h
n-Pentane	NC5	9.315	4.846	4.154	107.500	4.500
n-Hexane	NC6	10.617	4.846	4.154	125.480	4.500
n-Heptane	NC7	11.880	4.850	4.150	143.910	4.500
n-Octane	NC8	13.170	4.850	4.150	162.350	4.500
2-Metilbutane	2MC4	8.032	6.350	5.480	106.690	5.915
2-Methylpentane	2MC5	9.316	6.360	5.500	125.120	5.930
2-Methylhexane	2MC6	10.594	6.360	5.460	143.560	5.910
2-Methylheptane	2MC7	11.789	6.390	5.440	162.010	5.915
3-Methylpentane	3MC5	9.257	6.220	5.483	124.900	5.852
3-Methylhexane	3MC6	10.558	6.353	5.483	143.250	5.918
3-Methylheptane	3MC7	11.782	6.370	5.467	161.670	5.919
4-Methylheptane	4MC7	11.856	6.805	5.467	161.600	6.136
3-Ethylpentane	3EC5	9.243	7.600	6.110	143.510	6.855
3-Ethylhexane	3EC6	10.553	7.650	6.300	162.060	6.975
2,2-Dimethylpropane	22DMC3	6.744	5.524	6.744	106.050	6.134
2,2-Dimethylbutane	22DMC4	8.031	5.612	6.744	124.350	6.178
2,2-Dimethylpentane	22DMC5	9.334	5.616	6.720	142.790	6.168
2,2-Dimethylhexane	22DMC6	10.600	5.618	6.743	161.230	6.181
2,3-Dimethylbutane	23DMC4	8.045	6.898	5.472	124.440	6.185
2,3-Dimethylpentane	23DMC5	9.304	6.975	5.448	142.700	6.212
2,3-Dimethylhexane	23DMC6	10.558	7.025	5.482	161.200	6.254
2,4-Dimethylpentane	24DMC5	9.203	6.259	5.414	143.260	5.837
2,4-Dimethylhexane	24DMC6	10.413	6.231	5.483	161.620	5.857
2,5-Dimethylhexane	25DMC6	10.608	7.550	5.471	161.620	6.511
3,3-Dimethylpentane	33DMC5	9.230	5.565	6.742	142.560	6.154
3,3-Dimethylhexane	33DMC6	10.560	5.608	6.744	161.020	6.176

Here the w-h ratio gives the probability of molecule to get inside the pores. Now we will see the curve distribution of various zeolites and will find out which one is suitable. Iori Shimada *et al.*, (2015) explained Rest all of the data will be collected later on from catalyst department and it will be checked on excel sheet then we will be able to find out the actual zeolite pore dimension which we can use (Table 2.6).

Fig 2.20 Pore size distribution of various Catalyst used



By calculating this volume multiplied by area we will be able to come to a conclusion of which pore dimension zeolite to be used which will be done later on.

2.12 Temperature/conversion and metal on catalyst

As the temperature increases the branching decreases. Both metal on catalyst and the reactor temperature decrease the branching as selectivity of carbenium ion decreases. Carbenium ion is formed by low activation energy after protolytic cracking. Also as the conversion increases the carbenium ion selectivity increases so the branched product increases as conversion increase (Fig 2.20).

Now since all these are found out we tend to see that the iso product formation is mainly from PAH to increase the conversion out and thus now our main emphasis will be on how to crack out these PAH, where they are found out in the FCC column and what are the schemes we can apply to crack them, so we intend to do a reaction modeling to show that the given molecules are cracked down.

CHAPTER 3

REACTION MODELLING AND METHODOLOGY

Now the point here comes that where we have to use this strategy in which we have to decide that which part of the fcc stream we have to access so that we get to break up those PAH's into BTX and mono aromatics, so we choose LIGHT CYCLE OIL and CLARIFIED LIGHT OIL in which the amount of DI-Aromatics constitute of about 55% and Mono-Aromatics about 15-20 percent and we intend to break it down, the required hydrogen we will get from naphtha fractions that will be discussed further.

But before moving forward to it we need to know about the constituents of molecules that will be there in the light cycle oil ,their structure the mechanism they will follow and about the hydrogen transfer that will take place in the reaction, so for understanding that we will first look forward to hydrogen transfer reactions.

3.1 Hydrogen Transfer reactions

Iori Shimada *et al.*, (2015) explained using generally for reduction of multiple bonds by hydrogen gas and a metal catalyst. Types as described .

- 1) Hydrogen movement, taking place within one molecule.
- 2) Hydrogen disproportion, taking place within same donor and acceptors.
- 3) Transfer hydrogenation, occurring between different donor and acceptor.

3.1.1 CATALYTIC TRANSFER HYDROGENATION

Reduction of multiple bond with the help of organic atoms with hydrogen donor in presence of zeolite.



Here the donor compound is DHx (its oxidation potential should be low so that hydrogen transfer can occur at mild conditions). At sufficiently high temperature (>300 degree c) even benzene can serve as acceptor and can be reduced to cyclo hexane. So the choice of donor is decided by ease of reaction and availability.

Cyclo hexene is preferred because of its readily availability and high reactive.

3.1.2 Hydrogen transfer as understood under fcc process

- **Olefin + Napthene** \rightarrow **Aromatic + Paraffin** This is only a part of transfer hydrogenation where hydrogen is transferred from a donor molecule i.e. the napthene to olefin to subsequently give Aromatic and paraffin respectively.

Want to reduce a 3 ring or 2 ring PAH compound, we have to take hydrogen from an outer molecule to selectively hydrogenate the 3 ring PAH at center of the ring and form a naphthenic Aromatic compound

3.2 LCO Upgrading techniques used till now

Now since we are going to upgrade the LCO or CLO we will first look upon all the techniques which are now being used in refineries worldwide or are in recent development so that we can have a look upon them and compare our process through not fully detailed description of those techniques will be given on.

So we start with the blending of raw LCO into Fuel oil and heating oil pool that does not have any future, E. T. C. Vogtab *et al.*, (2012) explained then comes the UOP UNIFONING process in which hydro treating of LCO is done to remove S compounds, but this requires high pressure and will lead to over saturation of aromatics, inefficient use of hydrogen and only modest cetane improvement, The next process that we take into account is the full conversion hydrocracking which is an alternative to conventional hydro treating which is a well-established commercial process, here the objective is to saturate multi ring to high blending product, but the problem here that comes is the product is highly naphthenic. E. T. C. Vogtab *et al.*, (2012) explained then the third process we take into account is the UOP UNICRACKING process which gives good results with a aim to achieve good hydrogenation of diesel fraction and preserve aromatics, but still this process requires hydrogen being costly and also high pressure.

The other non-conventional method used is the bio-catalyst liquid liquid extraction in which the hydrocarbon contacts with this catalyst in the aqueous medium and then we make it a polar compound, then the S, N, Aromatics are separated at a given point by stopping the degradation of aromatic compound at intermediate stage and exploiting the physical and chemical properties at that time. E. T. C. Vogtab *et al.*, (2012) explained the other method which was talked about is the use of delaminated zeolites as a catalyst support in which an external surface area of zeolite was being exploited to crack heavy molecules like di and tri aromatics, in this process a two stage equipment was used in which first the feed is hydro treated to remove the sulphur component and then the second process is cyprocess less amount of gas is being produced and is good for diesel selectivity, though we can use delaminated zeolite in our process if cost is beared and further experiments are needed to be done on it to check its productivity. Another effort was made SINOPEC in 2012 Where effort was made to saturate the multi ring PAH compounds where LCO was compared in three process where a convention method, LCO recycled to main nozzles mixed with fcc fresh feed and the third process in which LCO was injected to second RISER REACTOR, here we see a bit increase in the gasoline yield and we can use this method along with cracking to get our desired result.

3.3 Light Cycle Oil and Clarified Light Oil

As we are going to use Light cycle oil or Clarified Light oil, we are going to know about the molecules there structure and the boiling range.

Table 3.1 LCO and CLO boiling range

Molecule name	Boiling Range (degree Celsius)
----------------------	---------------------------------------

LCO RANGE

1) Tetralin	207
2) Naphthalene	218
3) Bi-phenyl	255
4) 1- Phenyl octane	260
5) Ace Napthene	279
6) Ace Napthalene	280
7) Flourene	293
8) Phenanthrene	332
9) Anthracene	339
10) Alkyl derivates of 8,9	<350

CLO RANGE

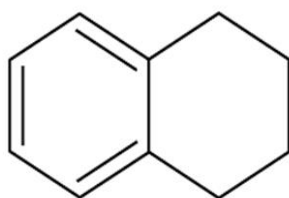
11) Flouranthene	375
12) Pyrene	404
13) Benz[a]anthracene	437.6
14) Chyrsene	448
15) Benzo[b]fluoranthene	481
16) Benzo[a]pyrene	495

17) Benzo[ghi]perylene 500

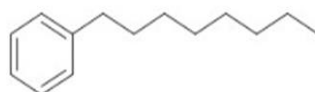
18) Indeno[1,2,3-cd]pyrene 536

The structure of these compounds are as follows

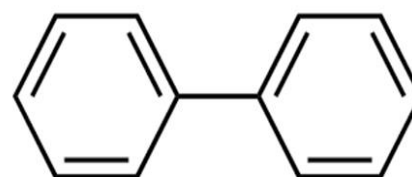
Fig 3.1 All AROMATICS related molecules in the range of LCO



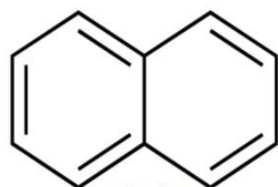
Tetralin



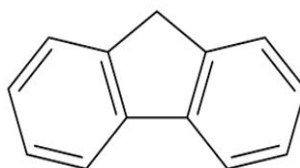
1-Phenyl Octane



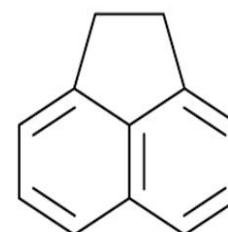
Bi - Phenyl



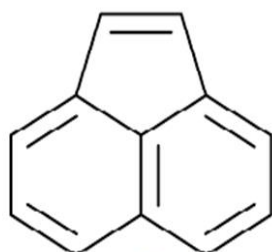
Napthalene



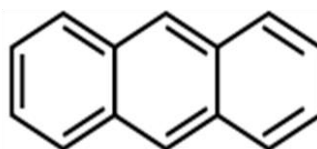
Flourene



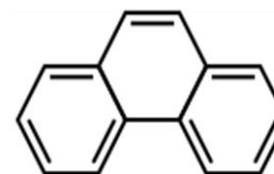
Ace-napthene



Ace- Napthalene

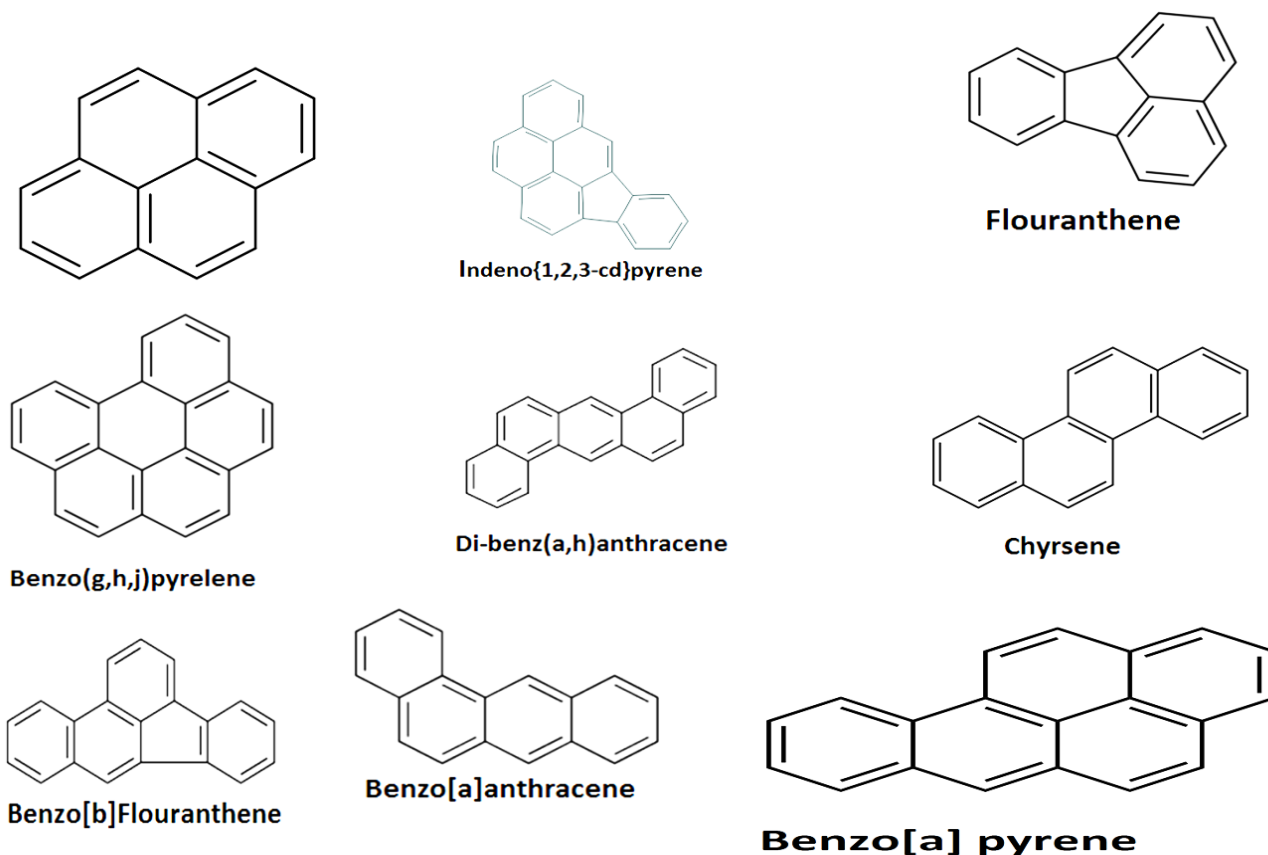


Anthracene



Phenanthrene

Fig 3.3 All AROMATIC molecules in range of CLO



Now if we want to see the mechanism of what these molecules follow then we have to check the similar amount of molecules and then the way forward of their class, we will get an idea of how other these type of molecules present in the boiling range of the light cycle oil may crack (Fig 3.1, 3.2).

3.3.1 MECHANISM

E. T. C. Vogtab *et al.*, (2012) explained The occurrence of un saturated compounds means it would initiate through the electrophilic attack of acid proton on the catalytic surface, will lead to formation of benzene and coke in most cases, because the benzene compound are rich in electrons and resonate to form a positive resonating species Benzylic Carbocation.

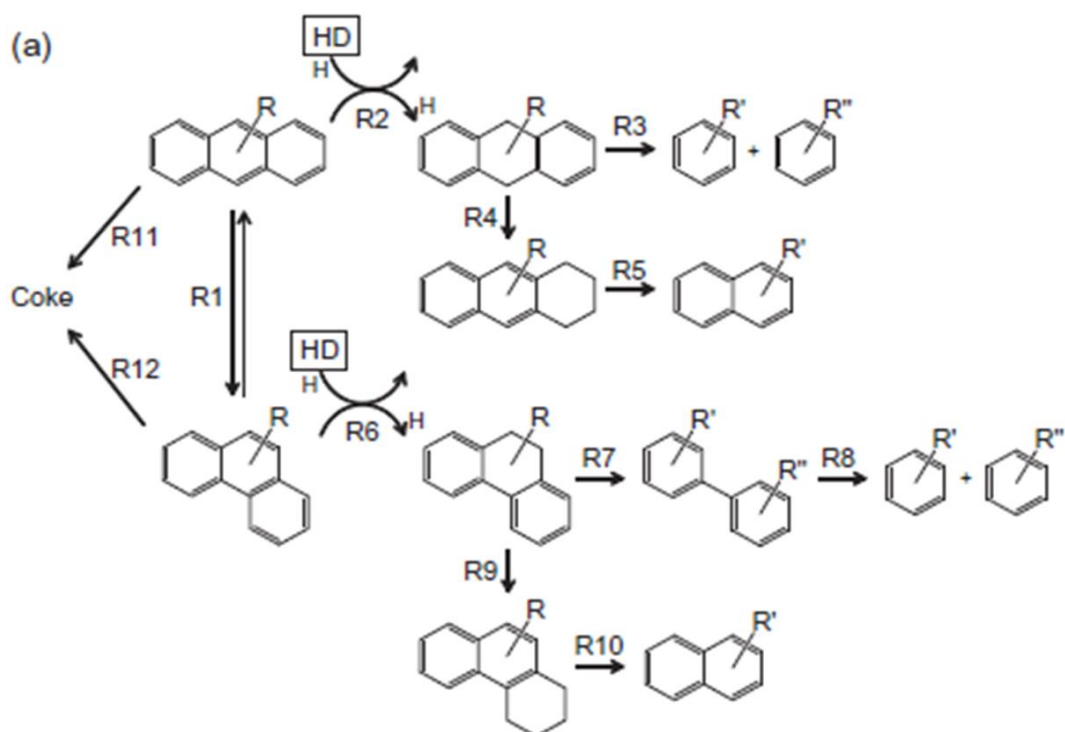
As for 1-PHO (phenyl octane) will produce C1-C2 light gases, BTX, Tetralin and biphenyl, since it is alkyl aromatic three routes are possible for it, dealkylation of benzene ring to yield Benzene and olefins, dealkylation of alkyl side chain to yield an olefin and alkyl benzene or paraffin and alkyl benzene, alkylation of intermediate alkyl aromatic to give intermediate alkyl aromatics and short olefin then the ring closing happens.

E. T. C. Vogtab *et al.*, (2012) explained Now if we take the case of naphtho-aromatics such as FLOURENE low light gases, Tetralin, Indane, biphenyl, and naphthalene .

Cracking is being promoted which makes phenanthrene the most important product by the dehydrogenation of saturated rings, that ring can be further opened upon and bi-phenyl bridge can be cracked on acidic sites, from other experiments it was found out that when Phenanthrene is cracked 9, 10 DPH is formed as a product meaning that the ring can be opened by the purely acidic mechanism initiated by the formation of benzylic carbocation.

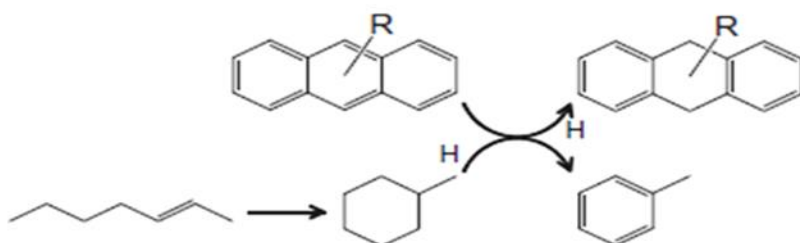
E. T. C. Vogtab *et al.*, (2012) explained In case for the Polycyclic aromatic compounds the susceptibility is there that the central ring will be attacked and there after the bi-phenyl bridge will be created and the given 3 and 2 ring PAHs will be Cracked .

Fig 3.4 Reaction mechanism of 3 ring PAH



The extra hydrogen required will get from naphtha by aromatizing olefins as well as hydrogen from the paraffin to olefin conversion. Here the hydrogen donor species in hydrogen transfer are considered to be cracking intermediate obtained from n-HD, eg olefin releases hydrogen atom for cyclisation and aromatization.

Fig 3.5 Hydrogen Donor compound



Here we can see clearly the olefin obtained from cracking paraffin cyclizes and gives hydrogen as it aromatizes that will be used in saturating the ring of PAH compounds (Fig 3.5, 3.4).

3.4 HYDROGEN DONOR MOLECULE

Now since we have to choose the hydrogen donor molecule we have got many options from the naphtha fractions we will have to analyse whether we will use Coker Naphtha, light straight run naphtha, heavy straight run naphtha, light FCC naphtha or heavy FCC naphtha. so we will observe these under the fcc conditions and then found out which the best we will also come to know about the mechanism which we are going to use to get the amount of hydrogen which will be required for cracking of the PAH molecule, for this purpose we will also select a scheme on how the naphtha fractions should be fed into the fcc reactor such that it gives us the best result possible to get the hydrogen from it and also

Now starting with the light straight run naphtha, four different schemes were chosen for the formation of olefins from paraffin's and olefin cyclisation through which we will get the required hydrogen, when we first cracked it with a gas oil on a Y zeolite (A) and ZSM-5(B) zeolite (75% and 25%) respectively, the result showed it did not crack but act as a diluent. E. T. C. Vogtab *et al.*, (2012) explained now the other three approaches were introduced

(a) Cracked at bottom most of the riser reactor, earlier than the gas oil injection zone, by feeding only naphtha into the reactor.

(b) By using a parallel riser and then contact the naphtha and catalyst

(c) Using stripper in the fluidized bed conditions

So starting with the separated riser reactor 0.9 wt. % conversion was obtained for catalyst A and 9% for catalyst B so we found it of no use, and we found out that even at very high cat/oil ratio carbon deposited on catalyst was very low in amount so to increase conversion fluidized bed reactor should be used so that to increase the contact time

So in the case of fluidized bed reactor the selectivity to light olefin was found good to be around 40% and the conversion be around 38%, in this case hydrogen transfer increased but amount of butane and propane were produced, high dry gas yield was there in this case as well.

E. T. C. Vogtab *et al.*, (2012) explained Now the third option to use bottom riser before the catalyst contacts gas oil feed, the conversion on catalyst B was around 36% but the main product was dry gas which we don't want but also there was high selectivity for propylene and butylene light olefins means less hydrogen transfer activity and more cracking as temp increases. The increase in amount of C7+ paraffin, olefin and naphthene will increase the selectivity to butylene and propylene that we will find in heavy straight run naphtha, though the check can be done on FCC naphtha .But since it is very costly and utilized well in refinery we need not to check it but a mechanism can be drawn out of it whether adding small amount of FCC naphtha will increase the reaction rate and help in olefin formation, the results of LSRN are given on next page.

Table 3.3 Comparison of products from LSR range

Operating conditions and results for LSR naphtha cracking

Test code	LSR 1	LSR 2	LSR 3	LSR 4	LSR5	LSR 6
Reaction scheme	Parallel riser		Riser bottom		Fluid bed reactor	
Catalyst type	A	B	A	B	B	B
Temperature (K)	823	823	923	923	823	823
Cat/oil ratio	13	36	34	37	12	30
Catalyst residence time (s)	1.1	2.2	2.1	1.8	30	30
Space velocity (h ⁻¹)	247	45	52	54	10	4
Dilution ratio (mol/mol)	0.2	0.2	0.2	0.2	0.2	0.2
Conversion (wt.%)						
n-Paraffins C ₅₊	0.2	9.9	35.7	43.4	–	–
Iso-paraffins C ₅	0	7.9	34.3	41.1	–	–
C ₆	0	4.8	29.6	37.8	–	–
C ₇	6.9	15.6	46.4	53.3	–	–
Cyclohexanes	4.0	19.6	48.0	54.9	–	–
Conversion to gas	0.87	8.96	28.35	36.49	36.12	68.22
Product yields (wt.%)						
Dry gas	0.12	2.11	11.64	14.83	9.09	16.60
C ₃ ⁼	0.36	3.65	8.00	12.63	9.32	12.04
C ₃	0.20	0.62	0.48	0.98	8.02	21.81
i-C ₄	0.10	0.19	0.26	0.20	1.74	4.53
n-C ₄	0.07	0.19	0.15	0.15	1.12	2.51
i-C ₄ ⁼	0.10	0.67	2.71	2.50	2.13	2.72
Total C ₄ ⁼	0.23	1.79	6.50	6.49	5.29	6.63
C ₃ ⁼ /C ₃	0.63	0.85	0.94	0.93	0.54	0.33
i-C ₄ ⁼ /i-C ₄	1.00	3.52	10.42	12.50	1.22	0.60
Benzene + toluene	0.83	1.06	1.41	1.91	–	–
Coke	0.16	0.60	1.47	1.36	1.54	4.15
Coke on catalyst	0.01	0.02	0.04	0.04	0.13	0.14

The selectivity for about 14 percent for propylene and 10 percent butylene, though there were more paraffinic gases for because of the high hydrogen transfer. Now if bottom of the riser approach is taken into account then the then the conversion on B is 43% and 18 % selectivity for propylene .The conversion is higher than the LSRN because of high olefin content and big length of chain in FCCN, the injection of FCCN direct into riser is the best option, but this process is not economic.

Table 3.4. FCCN cracking and the products obtained from it.

Conditions of operation and results for FCCN cracking

Test code	FCC1	FCC2	FCC3	FCC4	FCC5
Reaction scheme	Parallel riser			Bottom of the riser	
Catalyst	A	A	B	A	B
Temperature (K)	773	823	823	923	923
Catalyst-to-oil ratio	5.7	19	20	38	38
Catalyst residence time (s)	0.8	2.2	1.7	1.3	2.2
Space velocity (h^{-1})	789	86	106	73	43
Dilution ratio	0.2	0.2	0.2	0.2	0.2
Conversion (wt.%)	6.71	20.74	29.96	33.13	42.73
Product yields (wt.%)					
Dry gas	0.19	1.29	4.44	9.71	13.16
C ₃	0.05	0.67	0.61	0.57	0.84
C ₃ =	1.66	6.22	14.08	10.08	18.60
<i>i</i> -C ₄	0.62	3.48	0.34	0.58	0.17
<i>n</i> -C ₄	0.16	0.61	0.31	0.23	0.24
<i>i</i> -C ₄ =	1.17	1.70	3.81	4.08	3.25
Total C ₄ =	3.18	5.67	9.61	10.01	8.64
C ₃ =/totalC ₃	0.97	0.90	0.96	0.95	0.96
<i>i</i> -C ₄ =/ <i>i</i> -C ₄	1.89	0.49	11.20	7.03	19.12
Coke	0.85	2.80	0.57	1.95	1.08
Coke on catalyst	0.15	0.14	0.03	0.05	0.03
Quality of remaining gasoline					
Sulphur (%) reduction in gasoline	-	50	5	34	22
Research octane increment	-	1.5	0.3	3	2.8

Now if we take the case of FCC light naphtha ,it cracked more efficiently at 923 kelvin than LCN,if we do it at the bottom of the riser at the stripper zone will provide an advantage of decreased hydrogen transfer of coked catalyst and lead to high olefin cracking. There was an increase of 20% on overall conversion rate, with 84 wt. % of olefin transformed, 50 %of naphthene and 30 % of paraffin. At 723 k the olefins were cracked to paraffin's and aromatics, thus this means that the olefin conversion will produce hydrogen.

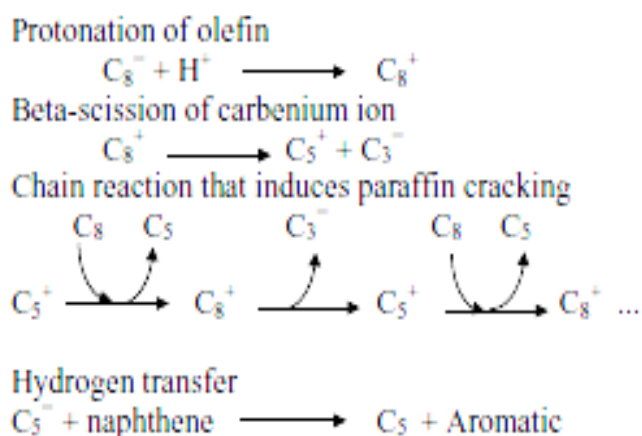
Reza *et al.*, (2003) explained low conversion of naphthenes is there but as the aromatic content has been increased this means that the naphthenes are also produced by cyclisation of olefins which is a desired process which will lead to further aromatization and providing us /

3.4.2 Mechanism

For cracking of the paraffin's there are two mechanism one is mono molecular and the other is bimolecular ,in the monomolecular mechanism a carbonium ion complex is formed by protonation on Bronstead acid site and it gives a paraffin and carbenium ion molecule which cracks to give olefins and acid proton on catalyst surface. Then carbenium ion formed in to go a bimolecular mechanism reacts with bigger paraffin's to form bigger carbenium ion and smaller paraffin and the carbenium ion further goes to form an olefin and carbenium ion.

Reza et al., (2003) The hydrogen transfer reaction is due to the bimolecular ones and thus as a result heavy molecules is that what we get, goes out to form aromatic compounds from naphthene, but this here we need to form hydrogen which will be released by paraffin to form olefins. So for that what we want is minimal acid site density that will lead to mono molecular transfer and thus lead to olefin formation and provide us with hydrogen. Dr. Cemal Ercan *et al.*, (2001) dealumination is one of the way to do it.

While if we see that the most reactive olefins are that which have more than 7 carbon atoms,naphthene with more than 7 c atom react extensively, now if we see the mechanism of how the olefin is initiated and further utilized to crack paraffin's into olefins .

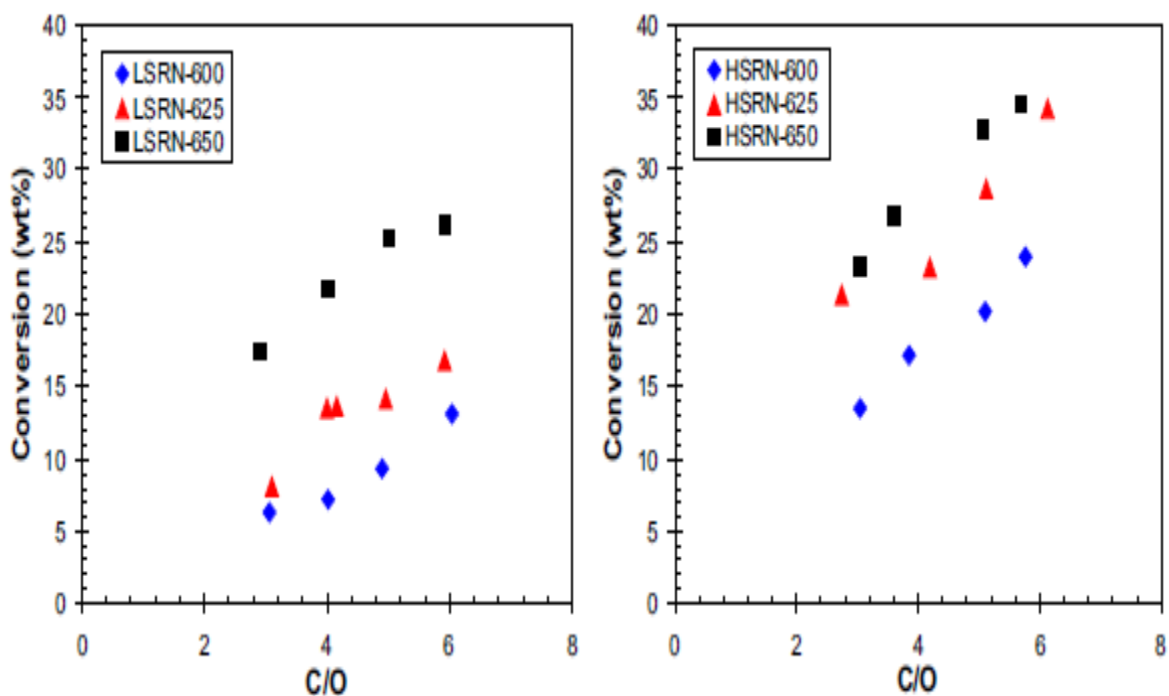


Scheme 1. C₅ paraffin formation from C₈ paraffins and olefins.

Fig 3.4.2 Reaction mechanism that shows olefins are initiators

Here we can see the reaction starts with protonation of an olefin, the olefin can act as an initiator and as we can see it cracks down to form a smaller light olefin and a carbenium ion, now it has got option to get beta scission but the chances are low, it can desorb as olefin or suffer hydrogen transfer forming a new C8+ ion, so by this large amount of olefin increase carbenium ion (Fig 3.8, 3.9).

Fig 3.8 LSRN & HSRN conversion on different temperatures at varying cat/oil ratio



Reza et al., (2003) explained the given image shows the higher conversion of HSRN which in term is preferred over LSRN which cracks very little as there are very small compounds to crack down.

Fig 3.9 Total yield of olefins from given LSRN and HSRN.

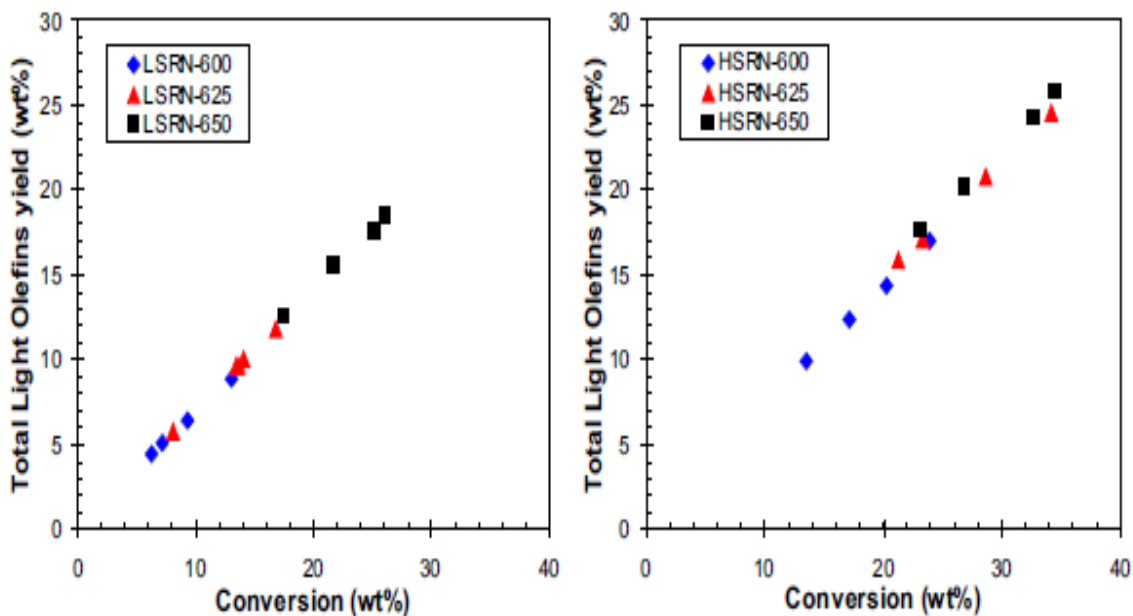
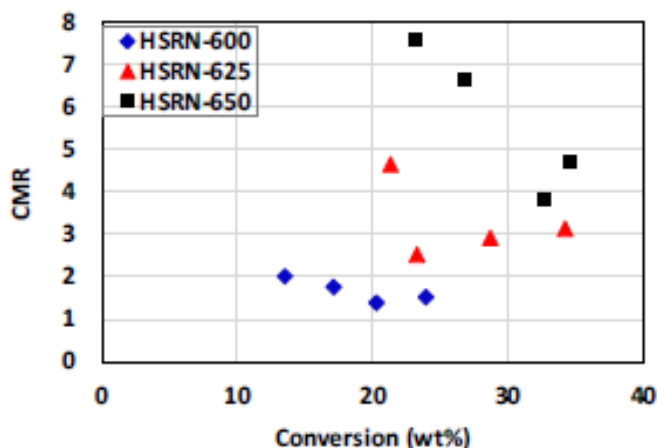


Fig 3.9 CMR index of Heavy Straight Run Naphtha



The CMR cracking index signifies that the single molecular cracking is more of a dominant in here as to the bi-molecular, and thus it is of worth using and the formation of hydrogen as the paraffin is converted to olefin molecules and thus will be used (Fig 3.9).

3.5 Technique for evaluating feed crack ability

Dr. Cemal Ercan et al., (2001) explained now since we have got to mix out 2 feeds the LCO/CLO and the HSRN we have to check out which version of it is the best i.e. in which quantity they must be mixed so that maximum cracking is been attained so for this purpose we ought to select the best combination possible and get the desired results. By finding out 2 properties of the feed we will find out the paraffinic, aromatic and naphthenic content and since in our LCO mechanism Naphtheneo Aromatics revert back to the 3 ring PAH, we sought out to lessen them and mix them in a proportionate manner. The method used is the N-D-M method.

3.5.1 K Factor

Reza et al., (2003) explained the K-factor tell us about how the feed is going to be cracked down. The K-factor checks out the relationship between the hydrogen amount in feed. This is done by using feed distillation and Specific gravity data logy, through this we get aromaticity relative to paraffin content of the feed. As K-value is high it shows grown Paraffinicty thus higher Crackability. A K-value < 11.9 the feed is rich in paraffins; a K-value less than than 11.0, refers to Aromatic feed. The known thing we have are VABP, Refractive index and Specific gravity, Aniline point, through this we will calculate out the rest

$$K_w = \frac{(\text{MeABP} + 460)^{1/3}}{\text{SG}} \dots\dots\dots (1)$$

$$\text{MeABP} = \text{VABP} + 2 - \left(\frac{(T_{90} - T_{10})}{170 + 0.075 \times \text{VABP}} + 1.5 \right)^3 \dots\dots\dots (2)$$

$$\text{VABP} = \frac{(T(10\%) + T(30\%) + T(50\%) + T(70\%) + T(90\%))}{5} \dots\dots\dots (3)$$

$$\text{MW} = 7.8312 \times 10^{-3} \times \text{SG}^{-0.09768} \times (\text{AP}, ^\circ\text{C})^{0.1238} \times (\text{VABP}, ^\circ\text{C})^{1.6971} \dots\dots\dots (4)$$

$$\text{X} = 2.51 (\text{RI} - 1.4750) - (\text{d} - 0.851) \dots\dots\dots (5)$$

$$\text{Y} = (\text{d} - 0.8510) - 1.11(\text{RI} - 1.4750) \dots\dots\dots (6)$$

Conditions:-

$$(\text{X} > 0, \text{A} = 211, \text{X} < 0, \text{A} = 721) \dots\dots\dots (7)$$

$$(\text{Y} > 0, \text{B} = 776, \text{Y} < 0, \text{B} = 1141) \dots\dots\dots (8)$$

Calculation of composition	
%Ca = AX + 3660/M	(% AROMATICS)
%Cr = BY - 3S + C/M	(% RING COMPOUNDS)
%Cn = %Cr - %Ca	(% NAPHTHENES)
%Cp = 100 - %Cr	(% PARAFFINS)

MW = Molecular weight

AP = Aniline point (degree c)

X = Factor 1

Y = Factor 2

d = Density

SG = Specific gravity.

MeABP = Mean average boiling point (degree F).

VABP = volumetric average boiling point(degree F).

T = Temprature at different concentration point.

Kw = Watson k.

So by finding this out we will get to know Kw equation (1), the MeABP equation (2), VABP equation (3), Molecular Weight equation (4) , X and Y factor equation (5,6) and conditions equation (7,8) that which feed is the best as earlier described the more will be the naphthenic feed the more it will tend to go towards the PAH compounds. So once after obtaining the given data we will have to check it on and get in finalized to see that how much of it may tend to form. We can obtain a table from the given data and thus therefore will then come to find it out the best feed.

3.6 Methodology

Here we tend to mix various mixtures of LSRN, HSRN and LCO, CLO after this we take them into different accounts and give it to the sample lab to get the properties like Refractive Index, Sulphur content, Aniline point and after that we rechange the various mixture feeds in the ratio

- 1) 3:1 (LSRN & LCO)
- 2) 4:1 (HSRN & CLO)
- 3) 5:2 (HSRN & LCO)
- 4) 3:4 (LSRN & CLO)

After this the mixture was tested and the contents were found out, given now we go to test it and then find out various contents . A table was been made out and all the contents were pulled inside it, giving now we know all the given datas here we sought to find out the other parameters and those will be calculated in the excel sheet using the K-Factor method and the N-D-M method.

CHAPTER 4 RESULTS AND DISCUSSIONS

So after calculating from the given properties we sought to find out the best feed combination mixture and from this the one with least no of naphthenic compound will give out the best forward reaction possible in forward cracking in the direction , as in case of light straight run naphtha the given evaluation was done and based on that the CLO compound was mixed with it

Table 4.1 Results of all different naphtha feedstock and their given values .

	FCCM	FCCM	FCC H	FCC H	FCC JR
LCO					
Distillation, vol%	D-1160, °C	D-1160, °C	D-1160, °C	D-1160, °C	D-1160, °C
IBP	268	309	244	250	250
5	370	310	325	331	331
10	386	336	347	355	355
30	425	387	400	406	406
50	450	418	429	437	437
70	483	447	462	469	469
90	530	498	625	610	610
95	542	522			
EP	546	584			
SG	0.8896	0.8896	0.9012	0.9033	0.9335
CCR (wt.%)	0.15	0.14	1.6	3.18	1.4
S (wt.%)	0.5	0.38	0.71	0.64	2
Asphaltene(wt%)	0	0	1.3	1.3	0.5
Watson K	12.35				
Asphaltene formed as %	1.08	1.08	1.08	1.08	1.08
CLO FCCM					
Distillation, vol%	D-1160, °C	D-1160, °C	D-1160, °C	D-1160, °C	D-1160, °C
IBP	256	330	218	222	222
5	322		320	324	324
10	365	349	338	345	345
30	415	386	360	368	368
50	442	412	382	387	387
70	462	441	410	412	412
90	513	506	430	435	435
95		581			
EP	521	670			
SG	0.979	1.076	1.0168	1.0215	1.08
CCR(wt%)	3.78	8.8	2.4	2.5	2.5
S (wt%)	1.13	1.26	1.7	1.9	1.9
CLO YIELD(wt%)	10.56	10.56	10	10	10
Asphaltene (wt%)	1.3	1.3	3	3	3

CALCULATION(LSRN)					
VABP(°C)	455	417	453	455	455
VABP(°F)	851	783	847	852	852
VABP(°R)	1310	1243	1306	1311	1311
MeABP(°F)	835	764	800	812	812
MeABP(°C)	446	406	427	433	433
MeABP(°R)	1295	1223	1260	1272	1272
Watson K	12.25	12.02	11.99	12.00	11.61
AP(°R)	660	645	646	647	632
	93	85	86	86	78
MW	450	384	441	446	439
<u>RI@20°C</u>	1.49	1.50	1.50	1.50	1.52
KV	0.0109	0.0154	0.0192	0.0203	0.0413
W	0.017	0.015	0.020	0.020	0.028
%Ca	12.68	16.00	16.40	16.79	25.97
Ca	22825.43	28799.54	15579.83	15947.50	24671.88
%Cr	34.42	36.93	36.55	37.06	39.53
%Cn	21.74	20.93	20.15	20.28	13.56
%Cp	65.58	63.07	63.45	62.94	60.47
CALCULATION(CLO)					
VABP(°C)	439	419	384	389	389
VABP(°F)	823	786	723	733	733
VABP(°R)	1283	1246	1183	1193	1193
MeABP(°F)	806	767	714	724	724
MeABP(°C)	430	409	379	384	384
MeABP(°R)	1266	1227	1174	1184	1184
Watson K	11.05	9.95	10.37	10.36	9.80
AP(°R)	612	583	585	586	576
AP(°C)	67	51	52	52	47
MW	404	356	310	317	312
<u>RI@20</u>	1.56	1.62	1.59	1.59	1.63
KV	0.0758	0.1506	0.1115	0.1142	0.1584
W	0.038	0.059	0.043	0.045	0.058
%Ca	41.51	74.87	59.58	60.44	79.66
%Cr	52.45	72.58	62.56	62.37	73.70
%Cn	10.94	2.29	2.98	1.93	5.96
%Cp	47.55	27.42	37.44	37.63	26.30

The result being found out that FCC JR was the prominent feed to be cracked up upon the given mechanism and we further intend to check it in case of HSRN as per now the given values of LSRN and CLO feed was pronounced. So when we tend to crack it we found out that the best given possible method of it is getting a heavy high range LCO or CLO to get more of a aromatic value rather as compared to a naphthenic value. This can be further used to detect the PAH cracking as the work goes on progress

CHAPTER 5 CONCLUSIONS

We started with the checking of the parameters that effect the iso-product formation and found many, but in the industry we are only allowed to make change through catalyst formation . There are various parameters of the catalyst that can be varied out to form a suitable catalyst, high rare earth content will be required to keep the unit cell size of the equilibrated catalyst constant, this will help us to promote iso-product formation, the use of small stable crystallites also provides a way through stable molecules which will lead to iso-product formation, we found out that when the PAH cracks down it produces iso – paraffin's and as our aim was to reduce the PAHs, which are very difficult to crack down and are found in LCO and CLO.

The unit cell size plays the utmost role here for the selection of iso –products and as we can see that the amount of iso-products produced will be more as the UCS increases, as the hydrogen transfer becomes more active than cracking.

Now we have to select the stream in the FCC which has PAHs, so the LCO and CLO are there .We found out the molecules and their boiling range which is to be found out, made a list and checked the mechanism part and drove out mechanism for both LCO and CLO.

So for this purpose a hydrogen donor molecule was required, we have to make various attempts on choosing the best possible hydrogen donor molecule ,so a series of deep investigation was done on various type of Naphtha's and among them the naphtha's being HSRN and LSRN which are the main naphtha's and are easily available at cheap price ,FCCN cannot be used as it is very costly, so we selected this naphtha and the LCO/CLO sample and then check out the feed crack ability on which one is the best found out that HSRN is the better one than LSRN as it has bigger molecules to crack down and form olefins from paraffin's by the mono molecular mechanism,

It was found out the one with less naphtho aromatic contents will be the best feed as it will not move to dehydrogenate itself and move towards the formation of PAH molecule instead of cracking, so out of all the feed molecules the mixture of LCO/CLO and Naphtha are to be analyzed and the best possible combination is chosen whether it is in ratio of 1:2 or 2:3. So now when done this ratio is being selected and the next step will be to choose a proper catalyst and test it in the MAT unit

The future scope if we see here is that first we have got the 2 streams to mix and once here their ratio is being found out we can then select the best possible catalyst and make them run through the MAT unit to check out how the results fare out , from the results we can make an analysis on the amount of di-tri aromatics and check out how much PAH is cracked, through our reaction model prediction and mixture of 2 streams it seems obvious that the molecules of PAH will crack in FCC condition and will break down LCO and CLO to lighter products .

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