STUDY OF FLUID CATALYTIC CRACKING CATALYST ADDITIVES FOR YIELD ENHANCEMENT

A THESIS

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ABSTRACT

Increasing refinery capacities and diminishing sweet crude reserves has given rise to processing of sour crudes containing sulphur, nitrogen and other impurities in enhanced proportions. Processing of high nitrogenous crudes has detrimental effect on catalyst activity. High nitrogenous crudes which contain nitrogen in the form of basic nitrogen compounds i.e. pyridine, quinoline, aniline affect the acidic sites of the catalyst and eventually decreasing its activity.

It is desired that basic nitrogen compounds maybe removed for reducing its effect on the catalyst selectivity. There are various methods available for removing the basic nitrogen compounds such as adsorption of nitrogen on a alumina-silica based catalysts, treating the FCC feed with mineral acids so that it forms water based salts and hydro processing of feed i.e. hydrodenitrogenation of FCC feed. There are various advantages and disadvantages associated with each and every method. In this work effect of basic nitrogen compounds on FCC catalyst activity was studied and a study had been done on few catalyst additives and its effect on catalytic activity in terms of conversion and selectivity. ZSM-5 and commercial BCA had been used as catalyst additives. In-house formulated BCA additives were tested for their effect on activity of the catalyst.

Key Words: Basic Nitrogen compounds, catalyst additives, catalyst activity, ZSM-5, BCA.

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CHAPTER-1

INTRODUCTION

FCC is an important conversion process in petroleum industries which plays a vital role in the profits in an integrated refinery and to the refiner. For most of the refiners the operation of FCC unit determines the profit made by the company. It is so estimated that there are around 400 FCC units globally with the capacity of around 12.7 MBPD. It is estimated that the 45% of gasoline world over comes from FCC units. Few major landmarks in the history of FCC process include

- Discovery which made it possible to catalytically crack heavy oil by the Friedal-Crafts Aluminum Chloride catalyst in mid-1910's
- In mid-1930's introduction of natural clays as catalyst enhanced cracking efficiency
- First commercial FCC unit started in Louisiana Refinery, NewJersy in 1942
- Development of microspheridical FCC catalyst in late 1940's
- Evolution of Bed Cracking Processes in 1950.
- Introduction of High Alumina Catalyst in mid-1950's
- Introduction of side by side design by UOP and invention of Riser cracking by Shell in mid-1950's
- Introduction of Zeolite content FCC catalysts in 1960's
- Development of USY and REY FCC catalyst by Mobil Oil in 1964
- Various additives for metal passivation and CO promoter introduced in 1970's
- First commercial use of additive was reported in 1983
- Introduction of two-stage regeneration for residues processing in 1980's.

In FCCU the catalyst is a micro spherical catalyst which is like a liquid when aerated by the gas. The main use of the FCC unit is to convert high boiling point fractions into the low boiling point fractions. It is simply the breaking of long chain hydro-carbons into smaller chain hydro carbons.

1.1 Process Description

The FCC process is a complex process which consists of various elements in the process which is shown as in Fig 1.1. They are described in the following sections as
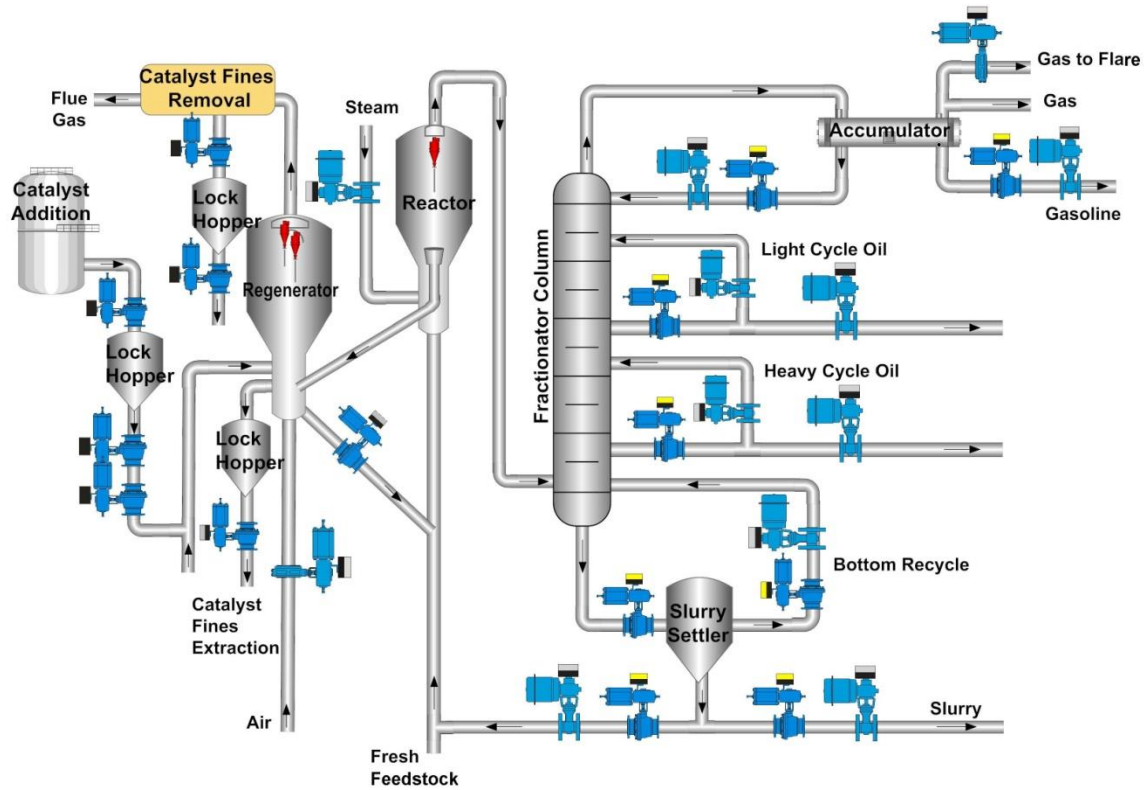
Fig 1.1 Process Flow in a typical FCC Unit.

1.1.1 Feed Preheat

The gas oil produced from the refinery or any other supplementary feed stock is sent to a surge drum, from where a steady flow is maintained into the charge pumps. This also helps in separating water that might be present in the feed stocks. Then the feed is generally heated to 260˚C to 370˚C. Feed preheater gives control over the catalyst-oil ratio which is an important parameter in the FCC process (Reza Sadeghbiege, 2000).

1.1.2 Riser-Reactor-Stripper

Reactor- Regenerator is considered to be the vital components of the FCC process. It is where the reactions occur in about 3.0 secs, before the catalyst and the products are separated in the reactor. The feedstock from the preheater is introduced into the riser where it comes in contact with the regenerated catalyst. As heat is absorbed by the catalyst in the regenerator, the heat energy in the catalyst heats the feed to its desired temperature. The general regenerated catalyst temperature ranging from 677 ˚C - 730˚C. As soon as the feed is vaporized the reactions take place and catalytic cracking occur in vapor phase. The expanding volume of the vapors helps in carrying the catalyst up the riser.

Steam is typically used for atomizing the feed. The minute oil particulates enhances the feed availability at acidic sites of the catalyst. The higher zeolitic content catalysts ensure that the cracking takes place in as short as 3 seconds.

1.1.3 Catalyst Separation

After passage out of the riser, the catalyst particles enter into the reactor section. In prevailing FCCU', the reactor acts as housing for cyclone separators. In most of the state of the art FCC units, the bulk catalyst from vapors is separated by employing cyclones at the end. FCCU use either a single or dual stage cyclone separators which helps in separating the catalyst particles from the product vapors. The catalyst is sent back to stripper through dip legs and flapper/trickle valves. The product gas is then directed to primary fractionating unit for product recovery. The typical efficiency of dual stage cyclone system is generally more than 99.995%.

1.2 Reactions involved in FCC Process

The FCC process cracks high boiling point, straight chain alkane (paraffinic) hydrocarbons into smaller straight chain alkanes, branched chain alkenes (olefins) and cycloalkanes (naphthens). The reactions involved in the process are as follows:
- Cracking
- Isomerization
- Dehydrogenation
- Hydrogen Transfer
- Cyclization
- Condensation
- Alkylation and Dealkylation

1.2.1 Cracking

The longer chain high boiling point fractions are cracked into smaller chain high value products. It is described as below:
- Paraffins are cracked into olefins and smaller paraffins.
  $$C_{10}H_{22} \longrightarrow C_4H_{10} + C_6H_{12}$$
- Olefins are cracked into lighter olefins (LPG olefins)
  $$C_9H_{18} \longrightarrow C_4H_8 + C_5H_{10}$$
- Naphthens are cracked into olefins and smaller cyclic compounds
  $$Cyclo\text{-}C_{10}H_{20} \longrightarrow C_6H_{12} + C_4H_8$$
- Aromatics undergo side chain cracking produces olefins and aromatics
  $$C_{10}H_{21} \longrightarrow C_5H_9 + C_5H_{12}$$

1.2.2 Isomerization

- Olefin bond shift

  1-C_4H_8 →trans-2-C_4H_8

- Normal olefins to iso-olefins

  C_4H_8 →iso-C_4H_8

- Normal paraffins to iso paraffins

  C_4H_{10} →iso-C_4H_{10}

1.2.3 Hydrogen transfer:

  Naphthens + Olefins → Aromatics + Paraffins

- Cyclo-aromatization

  C_6H_{12}+ $3C_5H_{10}$ →C_6H_6+ $3C_5H_{12}$

1.2.4 Trans-Alkylation/alkyl-group transfer:

  $C_6H_4 (CH_3)_2$+C_6H_6 → $2C_6H_5CH_3$

1.2.5 Cyclization of Olefins to Naphthens:

  C_7H_{14} → CH_3-cyclo-C_6H_{11}

1.2.6 Dehydrogenation:

  n- C_8H_{18} →C_8H_{16} + H_2

1.2.7 Dealkylation:

  Iso-C_3H_7-C_6H_5 → C_6H_6 + C_3H_6

1.2.8 Condensation:

  Ar-CH=CH_2 + R_1CH=CHR$_2$ → Ar-Ar + 2H
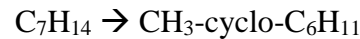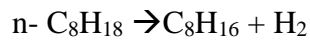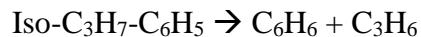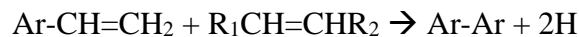
1.3 Products in FCC process

The typical feed stock Vacuum Gas Oil is cracked in the reactor and the products are obtained. These are as follows.

- Hydrogen, C_1's and C_2's and light gas
- Olefins -C3's and C4's (propylene, butylene, butadiene, etc. and LPG
- Gasoline C5+ high octane number component for gasoline pool or light fuel.
- Light cycle oil (LCO) which is a blend component for diesel pool.
- Heavy cycle oil (HCO).
- Clarified oil (CLO).
- Coke as by-product which provides the reactor heat demand.

1.4 New inventions in FCC Process

Fluid Catalytic Cracking had evolved over the years and there are few developments which had been done in the FCC process (Debashis Bhattacharya, 2013).
- ✓ Resid FCC Process (RFCC)
- ✓ Deep Catalytic Cracking (DCC)
- ✓ Petro FCC Process
- ✓ INDMAX Technology

1.4.1 Resid FCC Process

A RFCC unit expands the versatility and profitability of FCC process to crack a wider variety of feed stock. It can handle a wide range of feed stocks which include
- Conventional FCC Feed stocks
- Deeply Deasphalted Oil
- Atmospheric Residue
- Vacuum Residue

The RFCC is based on analogous reactor technology as traditional FCC unit and is embattled to process higher residue feeds which contain more than 4% Conradson Carbon by weight. It employs different approach which consists of a dual stage regenerator with additional facility for catalyst cooling so as to limit the coke production which is higher in RFCC. For the processing of residue feed stocks, the RFCC catalysts should contain more features than the traditional feed stocks. The catalyst structure must be designed to accommodate the large number of polycyclic compounds associated with the residue feedstock. In addition, the catalyst needs to be tolerant to the metals which are generally highly present in the residue feed stocks.

1.4.2 Deep Catalytic Cracking Process

DCC process is a conversion process which convert high boiling point hydrocarbon feed stocks catalytically to produce light olefins. This technology mainly targets the maximization of propylene and maximization of Isoolefins. The process outline of DCC is in resemblance to that of the orthodox FCC unit which consists reaction-regeneration section and a fractionator. Steam is used for stripping the coke deposited on the catalyst which is then sent to regenerator where air is brought into contact to catalyst, the coke is removed by the combustion.
The DCC process is generally operated in the temperature range of 520°C-580°C varying with crack ability of feedstocks and depending on the operating modes of DCC unit.
DCC can be operated in two modes
- Propylene Maximization mode

- Isoolefins Maximization mode

The DCC process can be easily shifted between the two modes of operation by changing the catalyst formulations and varying the operating parameters. The separation of products is as easy as it is in the conventional FCC unit.DCC lighter olefin products don't need hydro treating as impurity hydrocarbons are trace in them.

DCC catalysts should have higher activity, crack ability of bottoms and should be highly selective towards propylene.

1.4.3 Petro FCC

This process employs the technology for the production of petrochemical feed stock rather than the fuel (LPG, Gasoline) itself. This process uses a distinctively designed FCC unit which can produce great yields of light olefins and aromatics when used with complex aromatics.

This process uses a high conversion catalyst which is contacted at higher riser temperatures for short contact time.

1.4.4 INDMAX Technology

INDMAX FCC process produces more propylene, ethylene and butylene directly from heavy residues. It is commercially being operated IOCL Guwahati Unit. This process is highly flexible and can be adjusted depending on the demand and changes in feed stock properties.

This process is a typical FCC process which uses

- High cat/oil ratio about (15-25)
- Higher Riser outlet Temperature (ROT around 535˚C-540˚C)
- Higher riser steam rate
- Relatively lower Regenerator temperature.

In this process it is estimated to produce higher LPG about 35%-65% by wt. and also enhanced propylene (17%-25% wt.) yields and high octane gasoline (95+) as well

The particular catalyst used in this process is a propitiatory catalyst which has superior metal tolerance, higher propylene selectivity and low coke tendency.

1.5 FCC Catalysts

Catalysts are the major inventory in the FCC process and play a direct impact on the economics of the plant operation and profits made by the refiner. The introduction of zeolite had helped in achieving greater profits with lesser investment. The perpetually differing needs of market directed towards the innovation in the catalyst technology with minutest of investment. The zeolite catalysts are more active and shows better selectivity when compared to the conventional silica catalysts. The higher cracking efficiency and the larger liquid yield is due to the higher selectivity and activity of the catalysts. This had led to the revamping of the old FCC units so as to take the complete advantage of the zeolite catalysts.

The Fluid cracking catalysts are generally fine powders with APS of 75 microns. The present generation FCC catalysts consists of

- Zeolite
- Matrix
- Binder
- Filler

1.5.1 Zeolite

Zeolite (Reza Sadeghbiege, 2000) or otherwise termed as faujasite is the crucial component of FCC catalyst. The product selectivity and the activity of the catalyst is given by the zeolite and the performance of the catalyst essentially dependent on the quality of the zeolite.

Zeolite lattices have a linkage of tiny pores. The pore diameter of new generation FCC catalyst is about 8.0 A° and the internal surface area is around 600 m^2/g. The rudimentary block of a zeolite crystal is a unit cell. The distance between the repeating cells in the structure of the zeolite is unit cell. One unit cell in a commonplace crisp Y-Zeolite grid comprises of 192 framework atomic positons. The silica alumina ratio i.e. ($SiO2/Al_2O_3$) is around 5.Synthesized versions of naturally occurring zeolites are used as zeolites in the FCC process. The qualitative and quantitative performance of the catalyst is largely dependent on the zeolite properties. The zeolite is anticipated to hold its properties under extreme conditions. For e.g., in regenerators, the catalyst is exposed to thermal and hydrothermal treatments. In reactor, these are subjected to feed stock containing toxins such as V, Ni and other metals.

1.5.2 Matrix

Matrix (Reza Sadeghbiege, 2000) is the constituent of catalyst other than zeolite. The components of catalyst which have activity other than zeolite is called the active matrix. The source for the active matrix is alumina. The FCC catalysts uses amorphous alumina as matrix, however crystalline alumina can also be used. An active matrix adds to the overall performance of the catalyst. The Zeolite pores are not capable of cracking higher chain hydrocarbons, as the zeolite pores are too small to allow the diffusion of large molecules to the cracking sites. An active matrix should have a porous structure which allows hydrocarbons to diffuse in and out of the catalyst.

An active matrix provides the primary cracking sites. The acidic sites present in the matrix doesn't provide the selectivity as zeolites, but are capable to crack the large molecules which cannot enter the zeolite pores. The consecutive cracking takes place at zeolitic sites as the matrix precracks the heavy feed molecules. It acts as a trap to latch part of the vanadium and BNC's. The primary benefit of the active matrix is that it guards the zeolite from being deactivated due to these impurities.

1.5.3 Filler and Binder

Filler (Reza Sadeghbiege, 2000) is nothing but a clay which is integrated into the catalyst to dilute its activity. Kaoline is the most commonly used clay in FCC catalyst.

Binder is used as a glue to hold the zeolite, matrix and filler together. The binder is not expected to have any catalytic activity. The higher the zeolitic content, the more important is the use of binder.

The purpose of these two components is to offer physical integrity (density, attrition resistance, particle size distribution, etc.), a heat transfer medium and a fluidizing medium in which more expensive zeolite is incorporated.

FCC catalysts can be divided into two types

- Fresh Catalysts
- Equilibrium Catalysts (E-Cat)

1.5.4 Fresh Catalysts:

The catalyst consisting the zeolite, matrix, binder and filler is a fresh catalyst which has the catalytic activity of around 85%. Some of the properties of the fresh catalysts include Particle Size Distribution (PSD), Surface Area (m^2/g), Sodium content and Rare earth Content.

In commercial FCC units, a particular amount (depending upon the capacity of plant and other factors) of fresh catalyst is added every day and equal amount of E-Cat is removed. The fresh catalyst so added is eventually deactivated in the presence of steam in riser, stripper and regenerator.

PSD is a sign of fluidization attributes of catalyst. In general, the fluidization increases as of 0-40 microns particles increases, however a higher percentage of these particles also lead to catalyst loses.

Surface area another important property of the catalyst, the stated surface area is the collective surface area of the zeolite and matrix. The amount of nitrogen adsorbed by the catalyst determines the surface area of the catalyst. The SA is associated with the activity of the fresh catalyst. The zeolite surface area is proportional to the zeolite content in the catalyst.

Sodium (Na %) is one of the important property considered in the FCC catalysts. It has the detrimental effects as it causes deactivation of the zeolite content and shrinks gasoline octane. So it is desired that the Na % is kept as minimum as possible in the fresh catalyst.

Rare earth content in the catalyst is desired as it increases the activity of catalyst and hydrothermal stability. The catalysts may consist extensive range of Rare-Earth Content.

1.5.5 Equilibrium Catalysts

Equilibrium Catalysts (Reza Sadeghbiege, 2000) shortly called E-Cat is a steam deactivated fresh catalysts. The steam deactivation process results in decreasing the catalyst activity and

increasing the life of the catalyst. The E-Cat is generally used in large amount in commercial units. The E-Cat is used for the cracking of the Gas oil commercially. Fresh catalyst is a supplementary addition to the E-Cat consequently to overcome the catalyst losses and to make up the catalyst activity.

1.6 Catalyst Additives

For many years the regular practice of catalytic crackers operation is to add additive components for enhancing the performance of the cracker. Reduction of pollutants and the differing the FCC product yields and selectivities are the main advantages of the additives.
The additives generally used in the commercial FCC units (Reza Sadeghbiege, 2000) are
- CO Promoter Additive
- Sox & NOx Reduction Additive
- ZSM-5
- GSR
- Metal Passivation Additives
- BCA.

1.6.1 CO Promoter Additive

The Co-promoter is added to the vast majority of the FCC units to help the burning of CO to CO2 in the regenerator. The promoter is added to quicken the CO Combustion in the dense stage. The CO promoter facilitates the even burning of coke when there is a rough circulation between spent catalyst and air.
The active ingredients in the additive are platinum group metals. The concentration of platinum around 300-800ppm is typically distributed on a support. The use of the promoter is generally during the unit startups which help in improving the stability of the regeneration operation.

1.6.2 SOX Additive

The sulfur present in the coke when enters the regenerator is converted into SO_2 and SO_3. The mixture of these two gases is combindly called as SOX. The SOX additive is generally a metal oxide which is unswervingly added to the catalyst. The additive absorbs and chemically bonds the SO_3 in the regenerator which is then carried out to riser with circulating catalyst, where the reduction to by hydrogen takes place or it is regenerated by water to yield H_2S and metal oxide. The additive is more efficient in excess oxygen atmosphere as it promotes the formation of SO_3 over SO_2. The capturing effectiveness of the additive is higher in full combustion mode than in the partial combustion mode.
The NOX additive also uses the same principle where it forms NO and NO_2 which combindly called as Nitrogen.

1.6.3 ZSM-5

ZSM-5 is a Mobil's proprietary additive that consists of altered pore structure from Y-Zeolite. The pore size of ZSM-5 is smaller than Y-zeolite i.e. 5.0 A°. ZSM-5 helps in preferentially cracking of long chain, low carbon normal paraffins, as well as some olefins, in the gasoline fraction.

It is added to boost the gasoline octane and to increase light olefins yields. It is so accomplished by upgrading the low octane gasoline into light olefins and isomerization of the low-octane linear olefins into high-octane branched olefins.

ZSM-5 provides a lot of tractability to enhance octane number of gasoline and light olefins. With the introduction of reformed gasoline, ZSM-5 plays an important role in the production of isobutylene yields which is a feed stock for production of MTBE.

1.6.4 GSR:

Gasoline Sulfur reduction (F. Can *et.al.*2007) shortly called as GSR is an additive used for reducing the sulfur content in the gasoline. The sulfur components present in the gasoline are very stable (i.e. thiophenes, alkyl-thiophenes and benzo thiophenes). These compounds can be removed by the processes like hydro treating but the gasoline octane is compromised. Other desulfurization process requires other parameters and modification of FCC units which is non-desirable. Therefore the gasoline sulfur reduction additives implements a technology which uses a Lewis support on alumina (ZnO/Al_2O_3). It is estimated that the sulfur content is reduced by about 40% without effecting the other yields rather than slight increase in coke.

1.6.5 BCA

Bottom cracking additive shortly called as BCA is an active matrix which consists large pore (50 Å), non-crystalline, silica-alumina matrix with sufficient acidity to pre-crack larger molecules. The basic nitrogen compounds (Pyridine, Quinoline, Pyrrole, acrydine, etc.) present in the form of aromatics in the feedstock deactivate the catalyst by neutralizing the acidic sites.

BCA which consists of large pore matrix helps in cracking the long chain aromatics therefore preventing the loss of catalyst activity.

1.6.6 Metal Passivation Additive

The metals present in the feed stocks (i.e. Nickel, Vanadium, Sodium, etc.) get deposited on the catalyst, thus positing the active sites of the catalyst.

Antimony based metal passivation additive is generally introduced in the feed with the help of a carrier such as LCO to passivate the nickel compounds. These additive effects are generally

instant. Nickel is reduced by 40%-60% by dehydrogenation reactions, which takes place due to the additive forming an alloy with Ni.
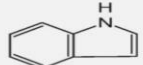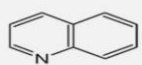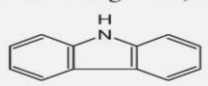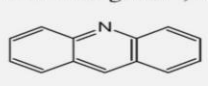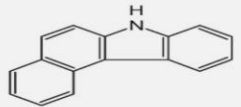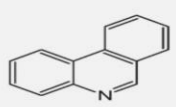
The antimony solution ought to be added in proportion to the nickel present in the feed. The optimum dosage normally responds to 0.3-0.5 on the E-Cat. Antimony preservation on the catalyst is about 75-80% without the recycle of slurry oil to riser.

1.7 Motivation for this work:

Increase of global refining capacities had given rise to new challenges to refiners throughout the world such as faster depletion of sweet crude reserves which led to processing of sour crudes (containing high nitrogen, high sulphur), higher refining capacities and stringent environment laws in the present era. The processing of sour crudes has an adverse effect on already existing refineries and the refiners has to come up with new technologies to overcome this problem and these are cost intensive. Even in the new refineries the residue generated in processing of sour crudes is comparatively high and the refiners are mandated to use more complex residue up gradation techniques (like RFCC). Processing of sour crudes has even effect on the existing methods (namely FCCU) i.e. the catalyst deactivation in FCC Unit. Catalyst in FCCU includes high inventory and the poisoning of catalyst is involves great expenditure to refiner.

Generally, the crude oil consists of a little amount of nitrogen, sulphur and other contaminants such as metals. But increase in the concentrations of these impurities pose a great challenge in refining and also on yield distribution.

Table 1.1: Nitrogen Hetero cyclic compounds present in the crude oil. (H.S. Cerqueira, *et.al*.2007)

Non-basic nitrogen heterocyclics	Basic nitrogen heterocyclics
Pyrrole $MW=67$ g mol^{-1}, $BP=130$ °C	Pyridine $MW=79$ g mol^{-1}, $BP=115$ °C
Indole $MW=117$ g mol^{-1}, $BP=254$ °C	Quinoline $MW=129$ g mol^{-1}, $BP=238$ °C
Carbazole $MW=168$ g mol^{-1}, $BP=355$ °C	Acridine $MW=181$ g mol^{-1}, $BP=346$ °C
Benzocarbazole $MW=216$ g mol^{-1}, $BP=385$ °C	Phenantridine $MW=181$ g mol^{-1}, $BP=349$ °C

1.8 Poisoning of Catalysts

High nitrogenous crudes (sour crude) contain basic nitrogen compounds which pose a great challenge to catalyst activity in FCC unit.FCC catalysts are zeolites, and the zeolites contain the active sites which are acidic in nature. The catalyst also contains matrix and binder along with zeolite. The actual phenomenon is the zeolites consist of small pores which are active sites of catalyst that acidic in nature, the basic nitrogen compounds (pyridine, acrydine, and quinoline derivatives) present in the feed stock (VGO or Vacuum Residue) of FCCU neutralize the acidic sites of the zeolites. Thus, eventually resulting in decline of catalyst activity, as a result of which the overall efficiency of FCCU is reduced. Although nitrogen poisoning is temporary and the catalyst activity can be retrieved with subsequent methods, the economics of the refinery is greatly affected as FCC directly has a great impact on the profits of the refiner.

1.9 Mitigation of poisoning of catalysts

There are methods (Robert B.Long, 1983) for the exclusion of basic nitrogen compounds from the crude oil:
1. Hydro treating: This method is a well-known method and widely used in the petroleum industry which involves hydro de-nitrogenation of crude to decrease the nitrogen content.
2. Use of Adsorbents: The adsorption method uses selective solid acidic adsorbents which help in removal of basic asphaltenics from the feed stocks (Robert H. Smit, 1978). This method is used for sync crude denitrogenation.
3. Solvent Extraction: Use of Immiscible solvent to extract nitrogen compounds. This method is used to remove nitrogen from shale oil
4. Neutralization: This method is a simple acid base reaction, basic nitrogen compounds are neutralized using acid additives. The products from the neutralization can be separated (Daniel J Curtin, 1981).
5. Use of Nitrogen Resistant FCC Catalysts. This method greatly reduces the cost involved in pretreatment process.

Every method afore mentioned has advantages and disadvantages. Most of the methods require an additional infrastructure which is likely to be difficult.

1.10 Objective of this work

The present work concentrates on the processing of nitrogenous crudes as in this work an attempt is made to use catalyst additives which in turn reduces the nitrogen effect on FCC catalyst. It is also aimed to study the effects of different catalyst additives on the activity. Various catalyst additives are studied in relative to the catalyst activity.

CHAPTER-2
LITERATURE REVIEW

Processing of high nitrogenous crudes has deleterious effect on FCC catalysts and it has been briefly discussed in the section above. The acidic sites of the zeolites get neutralized due to the presence of BNC's present in the high nitrogenous crude. There are various methods suggested by the researchers till now on removing the nitrogen compounds from the crude oil which has been discussed in the introduction.

The basic nitrogen present in the crude oil are namely: Pyridine, Quinoline, Pyrrole, Carbozole and other derivatives of pyridine and quinoline.

It is very well known that while processing the heavy crudes the significant objective is to convert the gas oil into lighter products. New generation FCC catalysts contain crystalline alumina silicates and the inorganic type matrix component. The zeolite influences the cracking and the matrix provides the stability for the particle and may also contain the active sites useful for the heavier hydrocarbons. (Russel R. Krug, *et.al.*, 1978)

The deactivation of the catalyst by nitrogen compounds is nitrogen poisoning of the catalyst.

2.1 Uses of Catalyst Additives.

The use of catalyst additives is an easy method which doesn't require an additional infrastructure or isn't cost intensive. The selective additive can be added to the catalyst directly as such. It has increased the flexibility of the FCCU over the years.

Catalyst Additive can be anything for e.g. Penatasil catalyst i.e. ZSM-5.

The other available additives are GSR, BCA and many other.

2.1.1 Uses of ZSM-5:

ZSM-5 stands for Zeolite Soccony Mobil-5 is a catalyst which belongs to a family of zeolite catalyst. It is an alluminosilicate whose chemical formula is $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O$ (0<n<27). The pore size of ZSM-5 is about 5Å and surface area of ZSM-5 is about 400 m^2/g.

ZSM-5 is used as additive to Fluid catalytic cracking Catalyst for various reasons.

1. ZSM-5 improves the gasoline RON. It boosts the gasoline octane number [8, 9]. Tests prove that the gasoline octane number is increased from 88 to 94.

2. It is used as additive for increasing the olefin yields which is a catalyst additive, mainly propylene yields are increased by the use of the ZSM-5.

According to G.Andrew Smith et al states that Penatasil zeolites has an ability to crack low octane gasoline materials out of gasoline fraction and leaving the higher octane material as such

The major difference between the two types of ZSM-5 is in its synthesis; both of them are isomers of each.

The modified ZSM-5 crystal generates a higher octane gasoline through isomerization, but with a lower loss in the gasoline pool than that with conventional ZSM-5.

2.2 EFFECT OF ZSM-5

The previous works using the above mentioned catalyst additives are discussed below:

The work done by (Xinjin Zhao *et.al.,*1999) by using the ZSM-5 as additive, the first 2% of additive provided the increase in 30% of propylene yields in comparison with the base case without any additive. His work states that by increasing the additive percentage to 32% there is a great increase of propylene yields from 4.6% to 11.1% which accounts for increase in propylene yields by 150%. The effect of riser output temperature was also studied and is reported that the effect of temperature on propylene yield is negligible at constant conversion. But the higher temperatures provided larger yields because of increase in conversion. This is because of the reason that at higher conversion, the gasoline also cracks and contributes to the propylene and butene yields. There is a different trend observed in butene yields when compared with the propylene yields. The addition of 4% additive yielded an increase of 25% butene increment, but it didn't reach the highest, though the incremental yield after 10wt% additive is negligible. The other product which has an incremental effect is ethylene with increasing ZSM-5 concentrations and the temperature.

The effect of propylene booster additive was studied by (Yannick Mathieu *et.al.,* 2012) on the yield pattern. The propylene booster additive is ZSM-5 zeolite which is added to the USY equilibrium FCC catalyst. It is stated that the use of ZSM-5 additive, increases the LPG selectivity, but at the cost of gasoline (lighter gasoline yield) and a bit to the LCO pool. It is also stated that the nature of the feed stock can have effect on product yield pattern. The results depicted here in this work states that the yield of C_2 to C_4 alkenes and olefin to paraffin ratio increased at the constant conversion level when ZSM-5 is used. C_5 alkenes didn't have great impact by the addition of the additive. By the addition of 10% wt. of additive has a great impact on the gasoline composition and hydrocarbon distribution. It is observed that proportion of aliphatic compounds particularly C_5+ olefins is strongly minimized by the use of ZSM-5 additive and increasing aromatic compounds by reducing the naphthenic-aromatic content. It is stated that the ZSM-5 consumes lighter gasoline olefins (C_6-C_7), for the production of LPG olefins. It is also concluded from his work that the inclusion of ZSM-5 to the USY equilibrium catalyst will have neutral or more probably a detrimental role on the LCO pool.

Another work of ZSM-5 additive by (J.Scott Buchanan, *et.al.,*1996) states that there is an increase of propylene yields by three times by the addition of 25% wt. of additive and the butene yields are raised by about 60%. By the addition of 25%wt of additive there is a negative impact on gasoline yield. The gasoline yields are dropped by 8-12% depending upon the base catalyst used i.e. RE-USY or USY. It is because RE-USY catalyst has more selectivity towards less coking and gasoline selectivity than the USY. The RE-USY contributed 2-3% more gasoline as

reported under every conditions. It is also stated that for the virgin catalysts increase in temperature had a damaging impact on gasoline yield as it has reduced by 2-3%. It is concluded that at constant conversion, there is no considerable effect on coke selectivity. By the increase in temperature C_2 yields nearly increased twice from 3.0 wt. % to 5.4wt% for RE-USY base catalyst. However there is no significant increase in C_2 yields by the addition of ZSM-5 but a considerable shift in paraffin- olefin distribution is observed. There is a small increase in ethylene from 0.3-0.7 wt.%. The significant difference is observed in the C_3-C_4 yields as the propylene is increased by about 300%. The addition of additive wt. % of 25 has a positive impact on the butene yields as it is increased by the factor of 1.6. When the temperature is increased from 811K to 852K in the presence of 25wt% additive, the results don't reflect a great change. This increase of light olefins is due to the decrease in the gasoline as seen in rising the temperatures. The cause for the decrease of gasoline composition is that the cracking process will have a higher activation energy than bimolecular hydrogen transfer process which in turn increases the tendency of C_5 +(pentene and higher) to crack into lighter olefins rather undergoing hydrogen transfer and contribute into more stable gasoline range. And the other effect observed by (J.Scott Buchanan *et.al.*,1996) is the RON (Research Octane Number) of gasoline pool in the product had an incremental effect. His observations state that the USY generally gave octanes about 0.5 times higher than RE-USY. Adding ZSM-5 and increasing the temperatures had a significant rise in octane number. His studies were carried out at the addition of ZSM-5 25wt% and increasing the temperatures from 811K to 852K.

 (A.Farshi *et.al*.,2012) worked with ZSM-5 states that the addition of ZSM-5 increased the olefin yields by 37% and for propylene especially there is an increase of 72%. It is so stated by him that the addition of ZSM-5 is having positive effect for the base catalysts which have lower hydrogen transfer activity. Findings from his work state that the addition of 50% ZSM-5 by weight would increase the ethylene yield would reach 45% and propylene yield would reach 38%. According to the tests carried out him, he suggests that the optimum addition of ZSM-5 is between 13-23% by weight. He also states that the increase of temperature from 450°C to 550°C increases propylene yields, but increasing more than 550°C increases methane than propylene. It is also quite obvious from his work that the addition of ZSM-5 by 23% weight at high severity increases the propylene yields to 30%. It is so concluded from his work that the addition of ZSM-5 with appropriate Si/Al ratio will produce more propylene and methane. By adding ZSM-5 it will produce more propylene than methane however at high temperatures it is vice-versa as methane is produced more than propylene.

2.3 EFFECT OF BCA

Bottom-cracking additive is a large pore (50 Å), non-crystalline, silica-alumina matrix with sufficient acidity to pre-crack larger molecules. This additive is a very recent development in the FCC field, and only a few commercial trials have been done so far, most in gasoline-mode FCC units.

The research at Indian oil Corporation Limited (S. Mandal,*et.al.*,1998) used BCA as an additive for FCC catalyst and the results reported states that the middle distillate yields are increased by 2 wt.% (depending on the heaviness of the feed). The experimental results state that the TCO (Total Cycle Oil) yield increase with the addition of 5 wt. % BCA. It is also noted that the coke yields and bottom yields are reduced to minimum by 5 wt. % additive addition. However there is an interesting trend observed as the TCO yields sharply decreased and the coke yields increased with further addition. The increment of coke levels is sharper when compared to the decrease in the TCO. This helps in stating that the optimum level of BCA is 5%, where the TCO yields are higher and coke and bottoms are lesser. The reason for increase of TCO while reduce in coke and bottoms is observed to be the reduction in thermal cracking as the BCA ranged from (0-5 wt. %). In the absence of BCA or in the presence of a lower concentration of BCA, the bigger molecules get thermally cracked to mostly coke, dry gas, and CLO because they are prevented from entering into the zeolite pore for selective cracking. With the increase in BCA concentration, selective cracking of bigger molecules is enhanced and reaches an optimum concentration (about 5 wt. %) when the zeolite-to-matrix ratio encourages maximum catalytic cracking. With a further increase of BCA concentration, thermal cracking is predominant, which leads to increased coke and bottoms yield. The optimum concentration of BCA is dictated by the feed heaviness, the host catalyst composition, and the operating severity level.

(Yannick Mathieu *et.al.*, 2012) has studied the effect of BCA addition in various wt. percentages (0%, 25%, 50%, 75%, 100%) and the results are discussed. It states that the addition of BCA to the E-Cat has a deleterious effect on catalytic activity, though the shrinkage is relatively very small for the 25 wt. % addition level. At 4 g/g catalyst-to-oil ratio, it was observed that a relative decrease of about 7% of the crack ability of the feed when incorporating 25 wt.% of additive, while at 50–75 wt. % of additive level and for the pure BCA additive, the crack ability reduction reaches respectively 17, 22 and 29%. This negative impact of BCA is likely due to the dilution effect of catalyst and has its origins due to low denser acidic sites in the BCA. The results depict that the use of higher concentrations of additive is likely to favor gases (dry gases especially) and LCO (Light Cycle Oil) selectivity whereas the gasoline pool and HCO is negatively impacted. There is an increase in dry gases and coke selectivity which is consistent with the fact that the addition of a catalytically lesser active additive would lead to higher ratio of thermal to catalytic cracking than with the most active Ecat. The optimum addition of BCA level for the cracking of residue feedstock will directly depend on the overall zeolite-to-matrix activity ratio of the composed catalytic system and will be different according to the properties of the catalyst, composition, experimental parameters and required product selectivity.

2.4 COMBINED EFFECT OF ZSM-5 and BCA:

The combined effect of addition of ZSM-5 and BCA is studied by (Yannick Mathieu *et.al.*, 2012) and the results are concluded based on his observations. He studied the combined effect of additives to the USY E-cat during FCC operation. The additives are added in such a way that the ratios are 30/60/10 of E-Cat/BCA/ZSM-5. The observations he made are conclusive in stating

that the activity of the catalytic system is dependent on feed properties. The adjustments in pattern and magnitude of gases when using the composite catalytic system are analogous to the ones observed in the case of the only addition of ZSM-5 additive even if the BCA is also probably involved in the little but representative increase of the dry gases yield, due to the enhancement of the thermal cracking contribution when using high addition level of BCA additive. It is concluded that the qualitative increase in the gasoline pool and the C5–C7 to C3–C4 alkenes shift which is due to the use of the ZSM-5 additive is the same and the addition or not of the Bottom Cracking additive has no or negligible effect. However, the BCA present in the amalgamated catalytic system helped in increasing the bottoms favoring the LCO selectivity even in the amplitude of feed characteristic dependency. The deleterious influence of ZSM-5 over LCO which was observed in the case of only ZSM-5 addition is partially or mostly compensated by the addition of BCA. Finally, the combined use of BCA and ZSM-5 additives allows the advantage of the solitary beneficial effects of the additives which intern attributes to the activity. It is then made possible to use a catalytic system in the FCC unit which allows production of light alkenes and good quality diesel pool, producing less gasoline but high quality, and limiting the production of dry gases and coke selectivities. His study concludes that the Bottom Cracking additive has a less catalytic activity and cannot be use as individual FCC catalyst instead of FCC E-CAT.

CHAPTER-3
METHODS AND MATERIALS

3.1 Characterization of Catalyst:

The catalysts and additives which are used in this work are characterized by different methods. The methods used for catalyst characterization are
1. Thermogravimetry Analysis (TGA)
2. BET Surface Area Analyzer

3.1.1 Thermogravimetry Analysis (TGA)

TGA is done for the additives and the catalysts used in this work for determining the characteristics of samples that exhibit the mass loss due to decomposition, oxidation or loss of volatiles which is attributed to moisture content in the catalysts and additives.
TGA measures the weight change as the function of temperature and time in an inert atmosphere in presence of nitrogen.

3.1.2 BET Surface Area Analyzer

BET analysis is done for the additives and the base catalysts used in the work which helped in determining the specific surface area in m^2/g. Surface area measurement is a characteristic that helps to screen the activity and stability of catalysts. There are many methods to estimate the surface area and every method may yield different results. Most of the methods adopt the principle of isothermal adsorption of nitrogen. Either a single point or multipoint method is used to calculate the surface area. At Engelhard, the multipoint BET method is used to measure the surface area of the fresh catalyst and equilibrium FCC catalysts. It is also used as quality tool during synthesis of catalysts.
The method used to determine the surface area showed that the respondents used a single point technique or multipoint point technique.
Most respondents used a data points in the range of 0.05-0.30 P/P_0, only one point is used below 0.05 P/P_0. In either a single point method or multipoint method the isotherm points are transformed with the BET equation given as:

$$\frac{1}{W[(\frac{P_0}{P}-1)]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\frac{P}{P_o}$$

Where W is the weight of the nitrogen adsorbed at a given relative pressure (P/P_0) and W_m is the weight of the gas given to monolayer coverage and C is constant that is related to the heat of adsorption. A linear relation between $1/W[(P_0/P)-1]$ and P/P_0 is required to obtain the quantity of nitrogen adsorbed. The intercept and slope are used to find out the quantity of nitrogen adsorbed and compute the surface area. The surface area will depend on the method used and the partial pressures as well.
The results are discussed in the later section.

3.1.3 Feed characterization.

The feed used i.e. VGO is analyzed for the presence of total nitrogen and sulfur content present in it. This is done by using Total Nitrogen Total Sulphur Analyzer by THERMO FISCHER SCIENTIFIC.

Thermo Fisher Scientific developed the TN/TS 3000 and Sphinx series analyzers for the ultra-low level analysis of Total Sulfur and Total Nitrogen in petrochemical products. These analyzers measure both Sulfur and Nitrogen simultaneously, making this analysis in liquid hydrocarbons very efficient and sensitive. This application note describes the sensitivity, linearity and reproducibility of the Thermo Scientific Trace Level Total Sulfur/Nitrogen analyzer series in the range of 0 to100 ug/L.

The Thermo Scientific TN/TS 3000 Total Sulfur/Nitrogen Analyzer complies with the following standard methods for this particular application:

ASTM D5453: Standard Test Method for determination of Total Sulfur in light hydrocarbons, motor fuels and oils by ultraviolet fluorescence.

ASTM D4629 Standard Test Method for determination of trace Nitrogen compounds in light hydrocarbons by chemiluminescence

A stock solution of 1,000 mg/L Nitrogen (element source is pyridine) and 1,000 mg/L Sulfur (element source is thiophenes) in xylene is the basis for the samples. Diluting the stock standard results in a set of samples ranging from 25 μg/L to 1000 μg/L. The auto sampler injects each sample into the analyzer.

The results include the mean integrated detector signal, the standard deviation and the relative standard deviation of the ten integrated detector signals per sample.

3.2 Experimental Setup:

The experiments are carried out in a Bench Scale Catalyst Testing Unit which is Micro Activity Testing (MAT) unit. MAT unit consists of a fixed bed reactor; the description of complete unit is as described below.

3.2.1 Description of Micro scale unit:

M/s ITS Corporation supplied the micro activity test (MAT) unit for performing the evaluation of FCC catalysts and additives. The unit is designed for 800 ^{0}C temperature. It is equipped with mass flow controllers; syringe pump, micro GC and CO-CO$_2$ analyzer. System is PC-PLC controlled with history information and trending facility of all process parameters.

The unit is having one fixed bed reactor. The reactor has been designed as per ASTM D3907. A thermo well has been located centrally in the reactor such that it can measure the temperature of feed just above catalyst bed. The reactor is located inside a three zone split furnace. Isothermal catalyst bed temperatures can be achieved using reactor furnace temperature control.
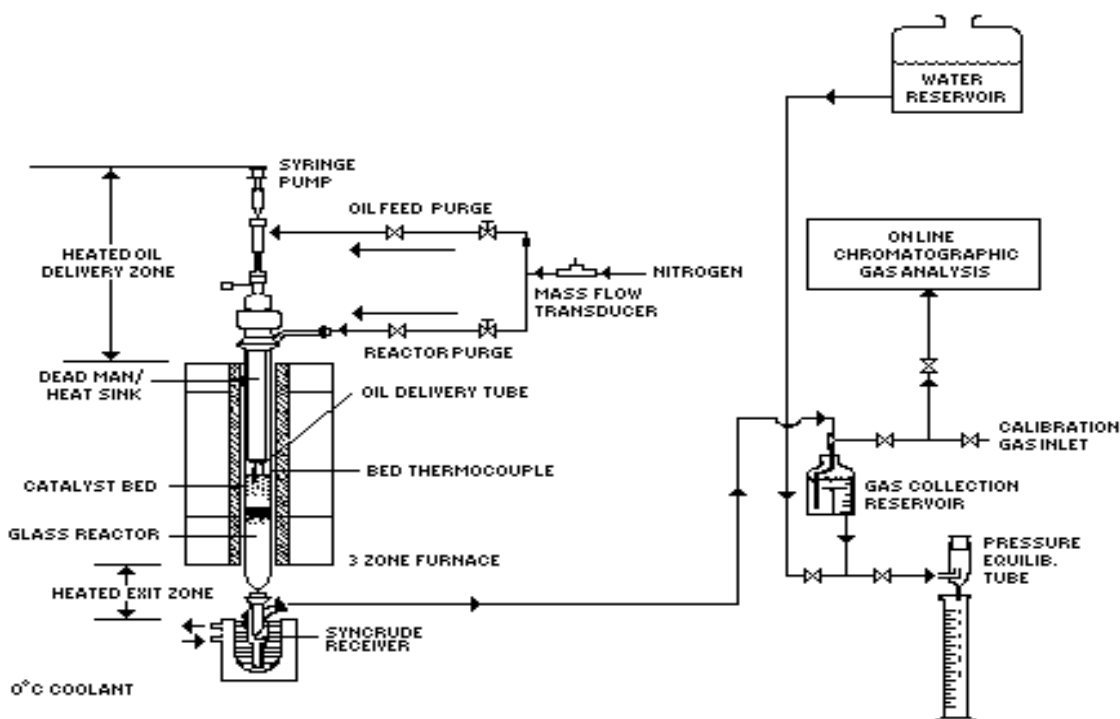
Fig 3.2.1: Description of Micro Activity Testing Unit (MAT)

3.2.2 MAT activity results

A sample of cracking catalyst and additive in a fixed-bed reactor is contacted with gas oil. Total catalyst quantity, including additive is 4 gms and the calculated amount of feed is contacted with fixed bed of catalyst for 89 sec. Product is passed through a chiller set at -15^0C where non condensable gases are separated and collected over water where volume of gas is measured through water displacement method. Weight of gas was calculated by standard excel sheet model. Gas is analyzed in 490 micro GC supplied by M/s Agilent. Liquid product is collected and weighed for mass balance calculations. Liquid product is analyzed by SIMDIS using ASTM method D2887. Mass balance was calculated as below.

Mass balance = (Liquid wt. + Gas weight+ coke)/weight of feed

3.3 Activity Studies

All the additive materials prepared in lab were tested in PC-PLC controlled micro activity testing unit (MAT) unit supplied by M/s ITS Corp. Chandigarh.

VGO from KR was used as cracking feed. Before starting the reaction feed line was rinsed with acetone and dried by air. Periodically insert was cleaned by purging air at reaction temperature for 1 hour at least once in 15 tests. Reactor and product receiver was washed thoroughly with acetone and dried. Once the reactor, insert and product receiver is cleaned, a plug of glass wool was inserted into the reactor. Total 4±0.05gms of catalyst is used and loaded into the reactor in a

free flowing manner. Plug of glass wool of smaller length was positioned above the catalyst bed. Wool plugs were not tamped excessively. Reactor feed tube insert was ensured to be free from deposits and the tip of the thermocouple is bent under the tip of the reactor feed insert. It is required to control oil preheat temperature accurately. Insert was placed in the reactor such that insert tube is between 10-50 mm above the catalyst bed. Reactor was placed in the furnace, different connections were made. Leak test was done by pressurizing the unit with nitrogen to keep Δp across the reactor 760mm Hg. After leak test run was started, in which furnace in turn reactor was heated by the ramp function which is already programmed. During heating nitrogen flow was kept at 60ml/min. To switch over from feed line to gas and vice versa multiport valve was provided. Product receiver was installed in the unit. Cracking temperature was set to 510 ± 2 ^0C. When the reaction temperature reaches valve position is switched over from nitrogen to feed line and after 30seconds hold time injection starts Syringe pump was set to deliver1.09$\pm$.03 Gms of feed in 89 seconds. Feed withdrawal time was set to 155 seconds. In the unit provision is for nitrogen flow or pure feed only. Nitrogen flow cannot be maintained during injection. Immediately after the oil addition, valve position is switched over to nitrogen flow at 60 ml/min to purge the reactor and product receiver. Reactor and product recovery system is purged with nitrogen for 15 minutes. For initial 250 seconds nitrogen is purged through feed insert and then switched over to reactor purging. A controlled temperature circulating bath was used for recovery of products. Circulating bath temperature was maintained at -15 ^0C. Product receiver is removed, sealed, dried and weighed immediately. Weight of liquid in receiver is recorded. Sample is analyzed in SIMDIS as per ASTM D2887 immediately, if not it is stored in a sealed vial in refrigerator.

The Product gas was analyzed using online 490 micro GC supplied by M/s Agilent.

The runs were reproducible and the material balance was approximately 99 wt. % for all cases.

The gases that are produced by the catalytic cracking are given below with the approximate weight percent.

3.3.1 Liquid analysis:

The liquid product which is collected from the experimental runs is analyzed for boiling point distribution using Gas Chromatography –SIMDIST.

The instrument is operated by the standard ASTM 2887 method.

The instrument is designed by PERKIN ELMER which consists of auto sampler, a column and septa. The GC is equipped with one FID and a capillary column

Column Specifications:

Length   : 6 m

Inner Dia: 0.53 mm

Resistance: 0.15µF

The temperature programme for oven and inlet conditions are as follows:

Analysis Conditions:

Carrier Gas: H_2

Injection Volume: 2.5µL
Detector temperature: 430˚C
Oven
Initial temperature: 40˚C
Maximum Temperature: 430˚C

3.3.2 Gas product Analysis:

The gas product collected in a gas reservoir is analyzed online by using Gas chromatography.
The instrument used is MICRO GC 490 by AGILENT which consists of three channels
Channel-1:
Packing: Molecular Sieves
Length: 10m
Carrier gas: Argon
Max.temperature: 180˚C
Conditioning @170˚C for 1 hour
Purpose: Estimates the composition of H_2, O_2, N_2, CH_4
Channel-2:
Packing: PPU
Length: 10m
Carrier Gas: Helium
Max.temperature: 180˚C
Conditioning @170˚C for 1 hour
Purpose: C_1-C_4 separation
Channel-3:
Packing: Al_2O_3
Length: 10m
Carrier Gas: Helium
Max.temperature: 180˚C
Conditioning @170˚C for 1 hour
Purpose: C_3-C_6 separation

3.4 Experimental Work:

As a part of research, experiments are done in the MAT unit with differing feed compositions
and different catalytic systems.
Firstly, a base case analysis is done with high nitrogenous feed (1200 ppm total nitrogen) and the
catalyst used is CCU-Ecat. The base case analysis is done for the low nitrogen feed (500 ppm)
and the results are discussed
The results are plotted in a graphical manner and are discussed in the results section.
The procedure for testing the catalytic activity remains same.

3.4.1 Effect of Basic Nitrogen Compounds

The effect of basic nitrogenous compounds on the catalytic activity was studied. The compounds used for these studies are pyridine and Quinoline.
Pyridine concentration is varied as (100, 250, 500 ppm) and the study has been done. Then the effect of quinoline is studied in different concentrations (100, 250, 500 ppm).
The results are plotted for each product and the yield pattern is discussed for the effect of BNC's

3.4.2 Effect of Additive on Quinoline Rich feed

The effect of ZSM-5 additive on the quinoline rich feed is studied in various concentrations (250 and 500ppm) and varying additive concentrations (5wt%, 10wt% and 10wt%, 15wt %) respectively.
The results are plotted for each product and the discussed for the addition of additive and the concentration of quinoline respectively.

3.4.3 Effect of ZSM-5 on High Nitrogenous Feed

The effect of ZSM-5 on high nitrogenous feed without any addition of model compounds (pyridine or Quinoline) is studied in various weight percentages (5wt%, 10wt %)

3.4.4 Effect of BCA on High Nitrogenous Feed

The feed a high nitrogenous feed and study is carried out to determine the effect of Bottom Cracking additive by varying the different weight percent (5wt%, 10wt %).
The results are plotted for each product and discussed in the next sections

3.4.5 Combined Effect of ZSM-5 and BCA

With the high nitrogenous feed, the combined effect of both ZSM-5 and BCA is studied by varying the weight percentages and the ratios in combination. (5wt%, 10wt %).
The results are plotted and discussed in the next sections.

3.4.6 Effect of in-house formulated additives

High nitrogenous feed is cracked with the in house formulated catalyst additives which are named as BCA-18, BCA-19 and BCA-20. The tests are carried out for the addition of 10 wt. % additive to the catalyst.
The results are discussed in the next section.

CHAPTER-4
RESULTS AND DISCUSSIONS

4.1. Catalyst Characterization

The catalyst which is used and the additives which are used had been characterized by the following methods:
1. Thermogravimetry Analysis
2. BET (Surface Area)
   - Thermogravimetry Analysis(TGA):
     The properties of the catalyst and additive used in this work are estimated using TGA and the results are tabulated as below:

Table 4.1.1 TGA analysis of the catalyst and the additives

S.NO	SAMPLE	MOISTURE CONTENT (30˚C-300˚C)	LOSS ON IGNITION (30˚C-995˚C)
1	BCA	5.37 %	12.81 %
2	ZSM-5	1.8 %	3.4 %
3	CCU E-CAT	8.0 %	14.4 %

   - BET Surface Area Analysis:
   The catalyst and the additives used in this work is analyzed for 6 point BET analysis and the results are as tabulated

Table 4.1.2 BET analysis of the catalyst and the additives

S.No.	Sample	Surface Area Analysis		
		MI PA (m^2/g)	MiPV (cc/g)	TPV (cc/g)
1	BCA	0	0	0.27
2	CCU E-CAT	116	0.05	0.12

| 3 | ZSM-5 | 119 | 0.05 | 0.08 |

4.2 Catalyst Testing

4.2.1 Effect of Basic Nitrogen Compounds

Basic Nitrogen Compounds present in the crude oil as discussed in earlier sections include Pyridine, Quinoline, Pyrrole and other quinoline derivatives.
The effects of these compounds are studied as a part of research and the results are tabulated.
The effect of basic nitrogen compounds is studied and compared with the low nitrogenous feed.
Few tests are carried out with the base catalyst i.e. CCU-Ecat without the addition of additive.
The feed characteristics and the experimental conditions are given below:

Feed	**VGO**
Feed total nitrogen	**500 ppm**
Cat/Oil	**3.66**
Reaction Temp.	**510˚C**

The results are tabulated as below:

Table 4.2.1.1: Yield for cracking low nitrogen VGO with CCU-Ecat.

Product Yield in wt.%	Low nitrogen BH VGO of order 500 ppm cracked by CCU-E CAT
H2	0.23
Dry gas	2.26
LPG	24.02
Gasoline	50.68
LCO	13.77
HCO	2.19
CLO	5.01
coke	3.71
Conversion	80.91

Table 4.2.1.2: Effect of pyridine on activity of FCC catalyst.

Product yield, wt.%	Without Nitrogen spiking	100 ppm Nitrogen(Pyridine)	250 ppm Nitrogen(Pyridine)	500 ppm Nitrogen(Pyridine)
H_2	0.22	0.20	0.18	0.18
Dry gas	2.35	2.38	2.09	1.85
LPG	19.82	16.51	14.42	14.36
Gasoline	43.35	42.94	36.34	35.16
LCO	19.73	20.84	20.87	21.46
Bottoms	10.76	13.41	22.48	23.18
coke	3.78	3.72	3.63	3.55
Conversion	69.52	65.75	56.65	55.10

Table 4.2.1.3: Effect of Quinoline on activity of FCC catalyst.

Product yield, wt.%	Without Nitrogen spiking	100ppm Nitrogen(quinolne)	250ppm Nitrogen(quinoline)	500ppm Nitrogen(quinoline)
H_2	0.22	0.19	0.16	0.24
Dry gas, wt%	2.35	1.91	1.75	1.41
LPG	19.82	12.31	9.20	9.21
Gasoline	43.35	38.99	31.93	31.14
LCO	19.73	22.38	22.75	24.25
Bottoms	10.76	20.62	30.68	30.30
coke	3.78	3.61	3.55	3.45
Conversion	69.52	57.01	46.58	45.45

The effect of Basic Nitrogen Compounds (BNC's) which are studied as a part of the study is plotted below.
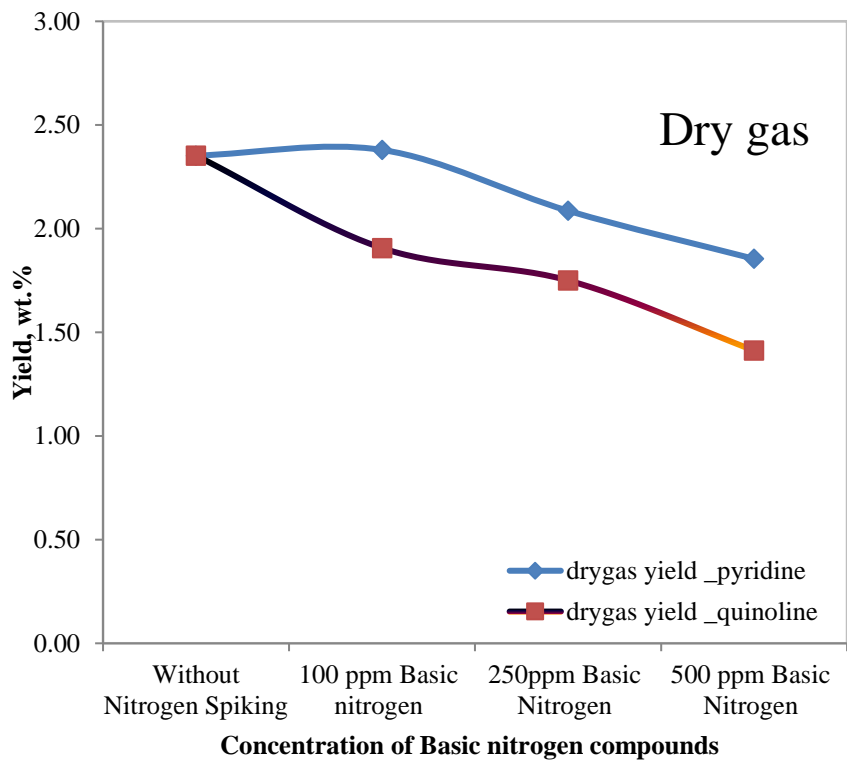
Fig 4.2.1.1 Effect of BNC's on Dry gas yield.
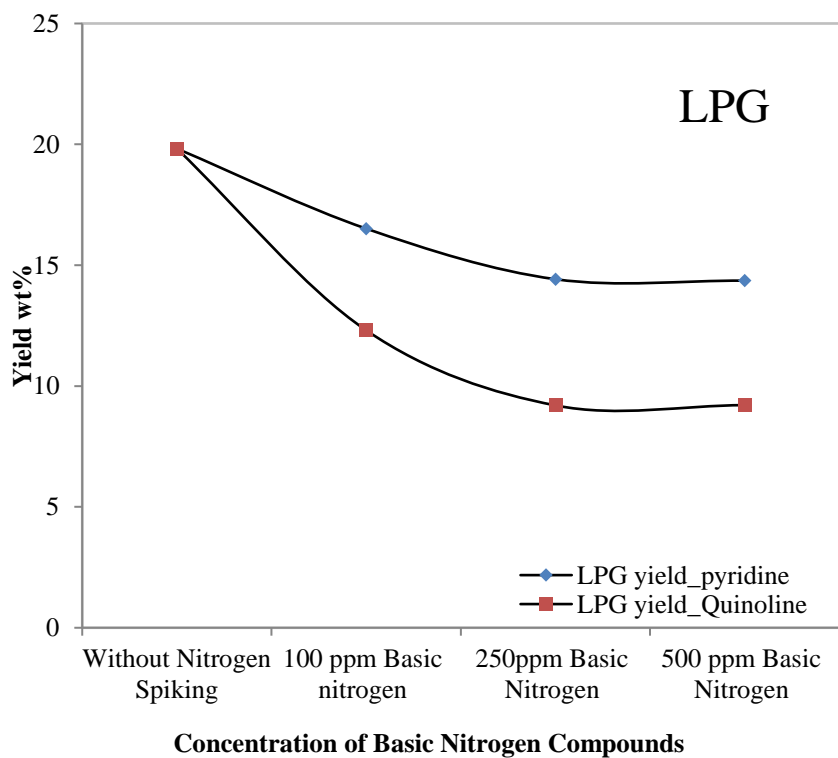
Fig 4.2.1.2 Effect of BNC's on LPG yield.
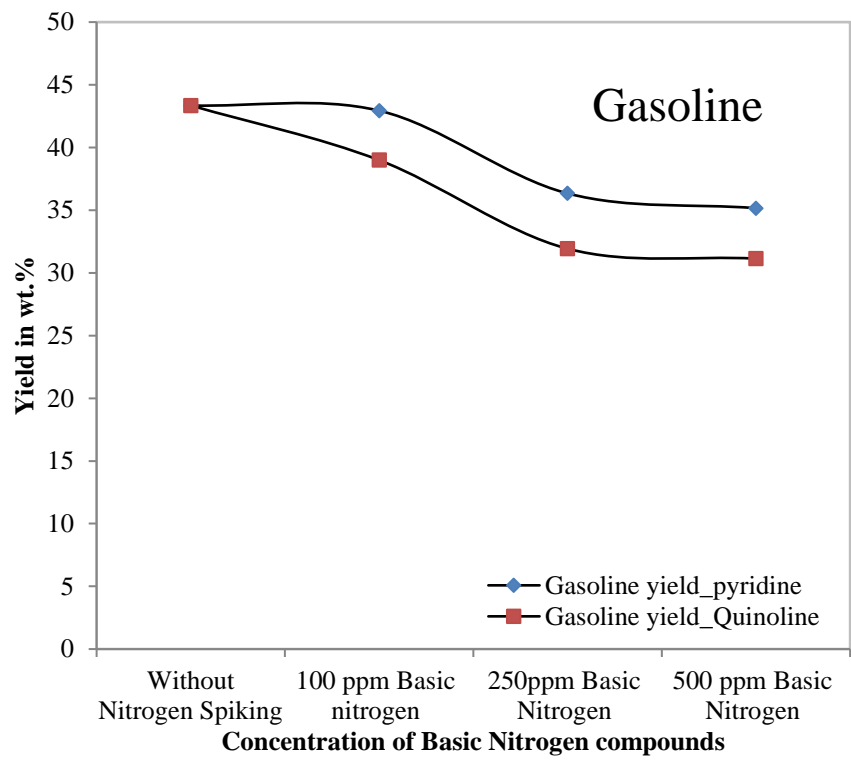
Fig 4.2.1.3 Effect of BNC's on Gasoline yield
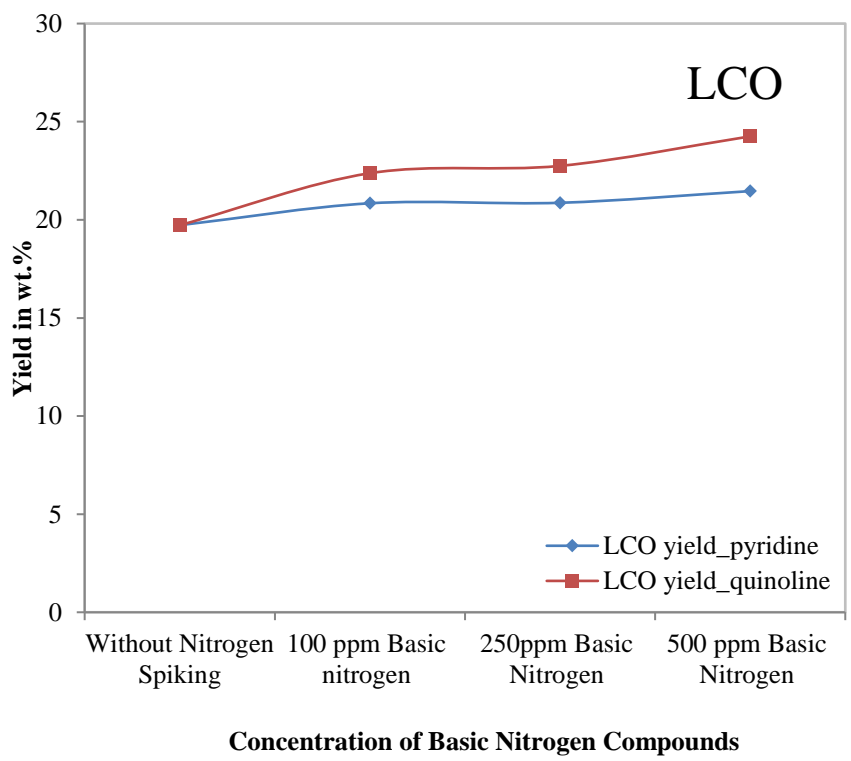
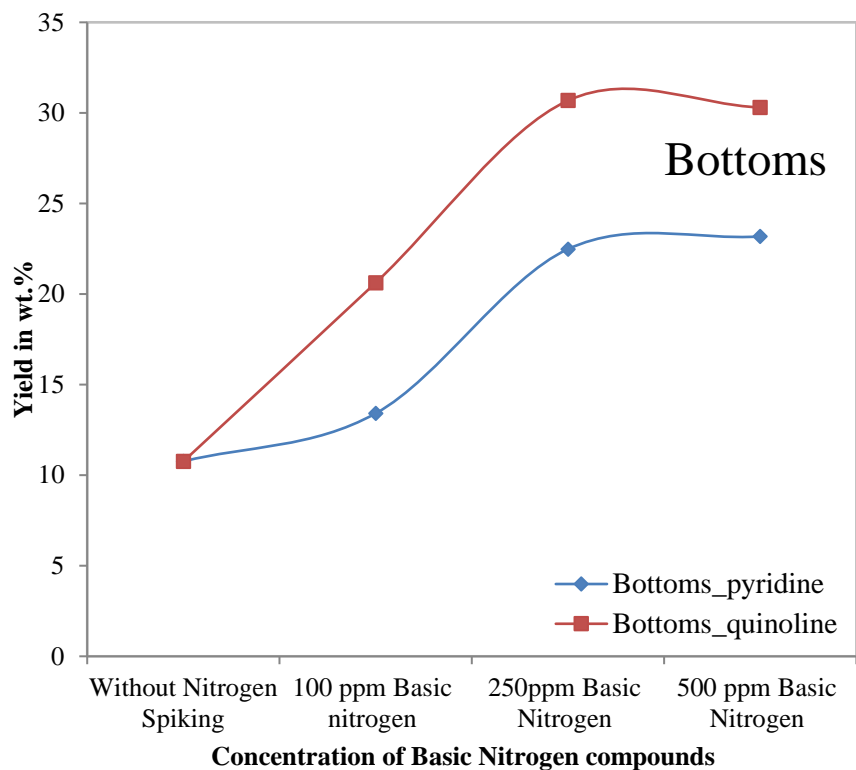Fig 4.2.1.4 Effect of BNC's on LCO yield

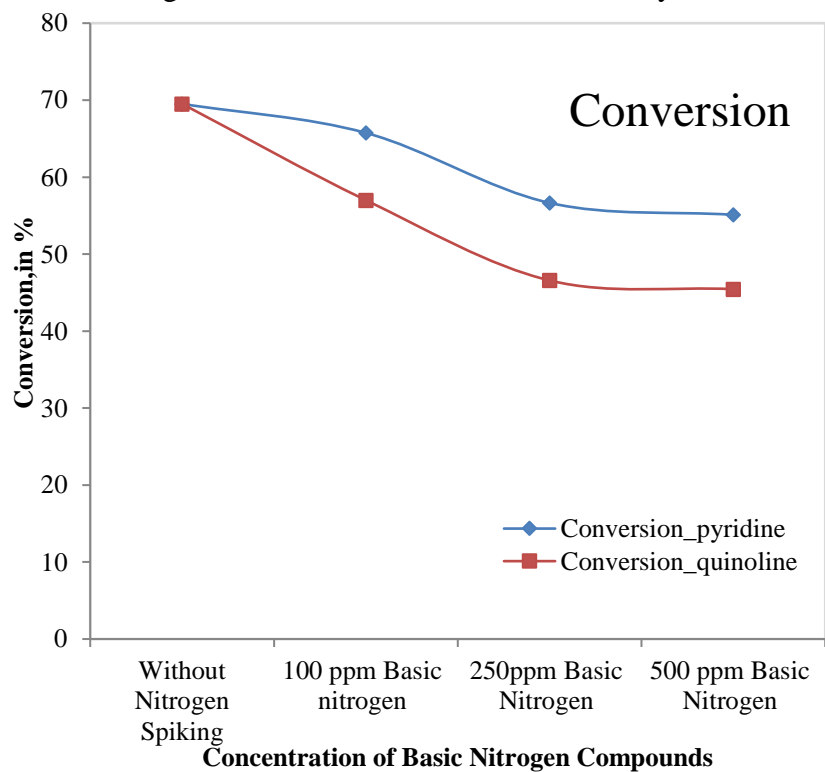Fig 4.2.1.5 Effect of BNC's on Bottoms yield

Fig 4.2.1.6 Effect of BNC's on Conversion.

The effect of the Basic Nitrogen Compounds (BNC's) i.e. Pyridine and Quinoline studied as a part of the study. It is telltale that the Basic Nitrogen compounds (Pyridine and Quinoline) has

deleterious effect on the catalyst activity. The active acidic sites of the catalyst were neutralized by the basic compounds present in the feed stock.

The pyridine is more basic than the quinoline; however the quinoline is more bulky than pyridine. This explains the contradiction of lower catalytic activity in case of quinoline than in the case of pyridine. In case of quinoline the loss of catalytic activity attributed to conversion is around 20% whereas in the case of pyridine it is around 14%.

4.2.2 Effect of additive on Quinoline rich feed

The catalytic activity is tested with the quinoline rich feeds i.e. 250 ppm concentration and 500 ppm concentration with the addition of catalyst additive i.e. ZSM-5 in different weight percentages. (5 wt. % and 10 wt. %) for both the feeds.
The feed characteristics and the experimental conditions are as follows:

Feed	VGO with Quinoline 250 ppm
Feed total nitrogen	1470 ppm
Cat/Oil	3.66
Reaction Temp.	510°C

Table 4.2.2.1 Effect of ZSM-5 on FCC Catalyst activity for 250 ppm Quinoline Feed

Product in wt.%	Without additive 250 ppm quinoline	Nitrogen concentration 250 ppm with 5 wt.% ZSM-5 and E-Cat	Nitrogen concentration 250 ppm with 10 wt.% ZSM-5and E-Cat
H_2	0.16	0.23	0.20
Dry gas	1.75	3.46	4.57
LPG	9.20	23.96	26.96
Gasoline	31.93	31.43	30.52
LCO	22.75	18.57	16.46
Bottoms	30.68	18.58	17.23
coke	3.55	3.75	3.82
Conversion	46.58	62.83	66.06

The feed characteristics and the experimental conditions are as follows:

Feed	VGO with Quinoline 500 ppm
Feed total nitrogen	1710 ppm
Cat/Oil	3.66

Reaction Temp.   **510˚C**

Table 4.2.2.2 Effect of ZSM-5 on FCC Catalyst activity for 500 ppm Quinoline Feed

Product yield, wt.%	Without additive 500 ppm Quinoline	Nitrogen concentration 500 ppm with 5wt.% ZSM-5 and Com.E-Cat	Nitrogen concentration 500 ppm with 10% ZSM-5 and Com. E-Cat
H_2	0.24	0.21	0.20
Dry gas	1.41	4.14	4.59
LPG	9.21	20.25	23.67
Gasoline	31.14	30.50	29.61
LCO	24.25	19.95	18.11
Bottoms	30.30	21.28	20.11
coke	3.45	3.67	3.71
Conversion	45.45	58.77	61.78
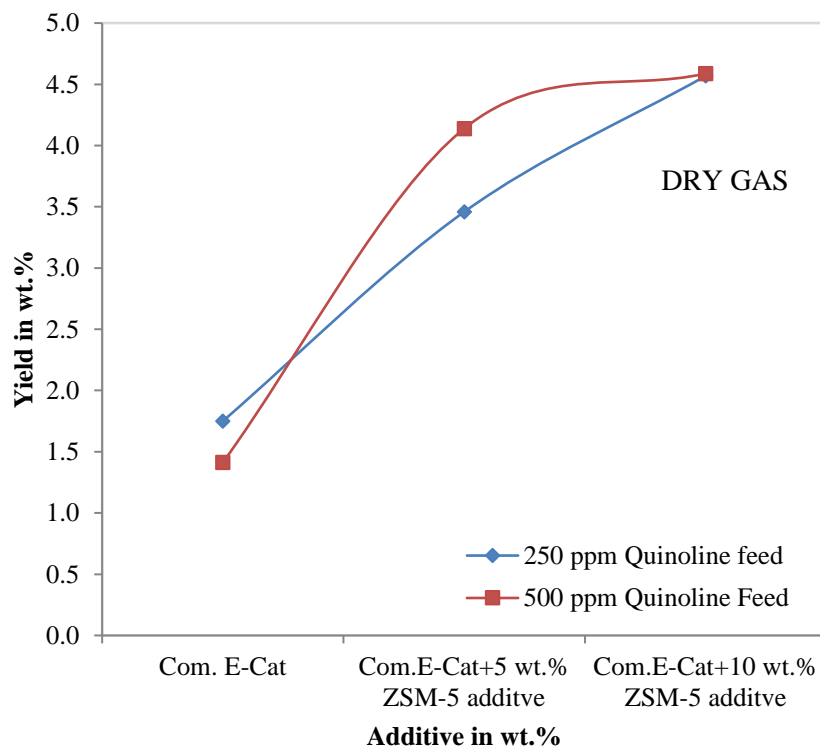
Fig 4.2.2.1 Effect of ZSM-5 additive on Dry gas yield for Quinoline rich feed
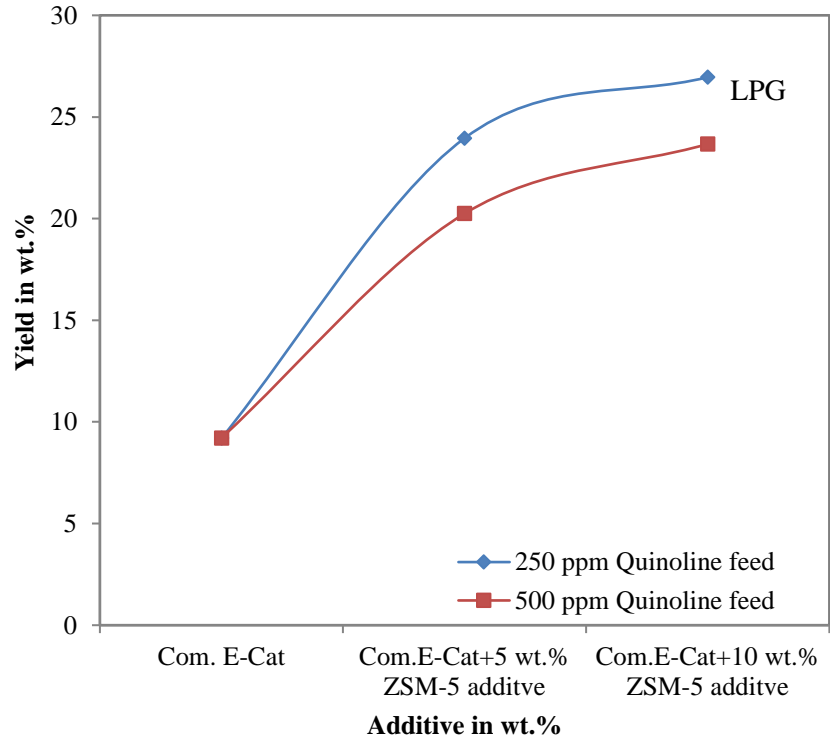
Fig 4.2.2.2 Effect of ZSM-5 additive on LPG yield for Quinoline rich feed
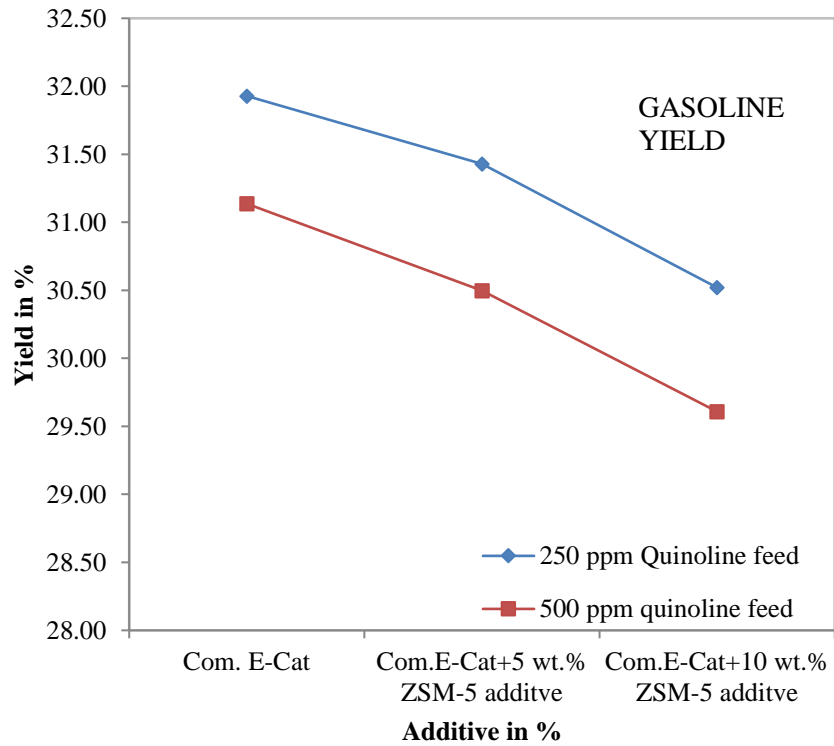
Fig 4.2.2.3 Effect of ZSM-5 additive on Gasoline yield for Quinoline rich feed
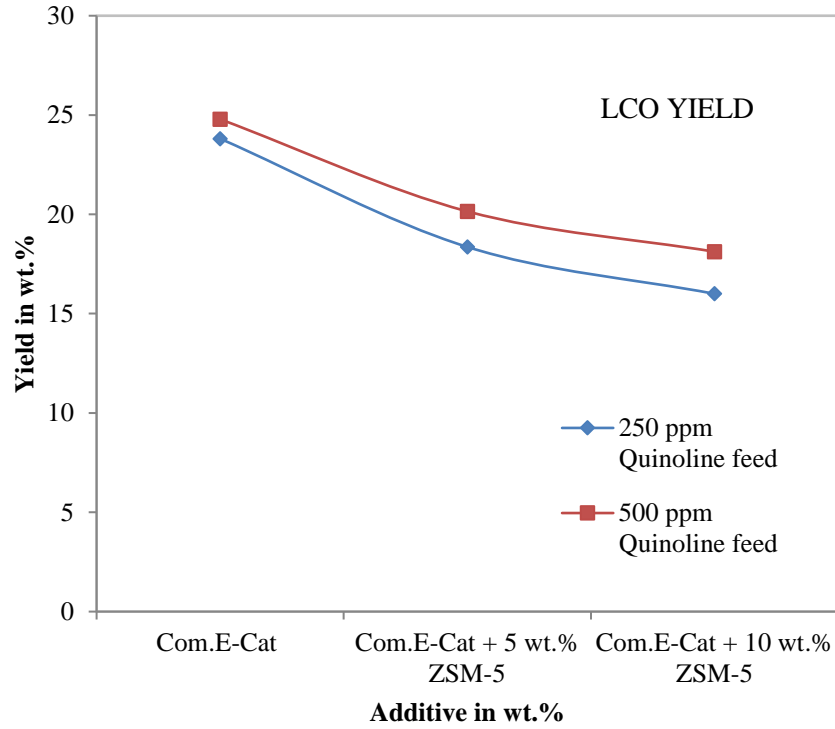
Fig 4.2.2.4 Effect of ZSM-5 additive on LCO yield for Quinoline rich feed
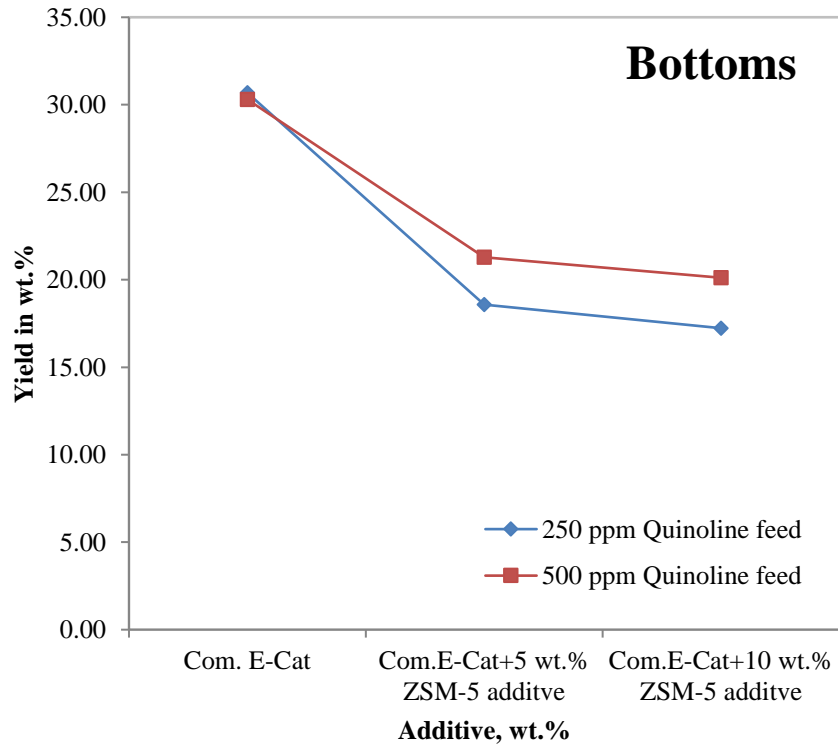
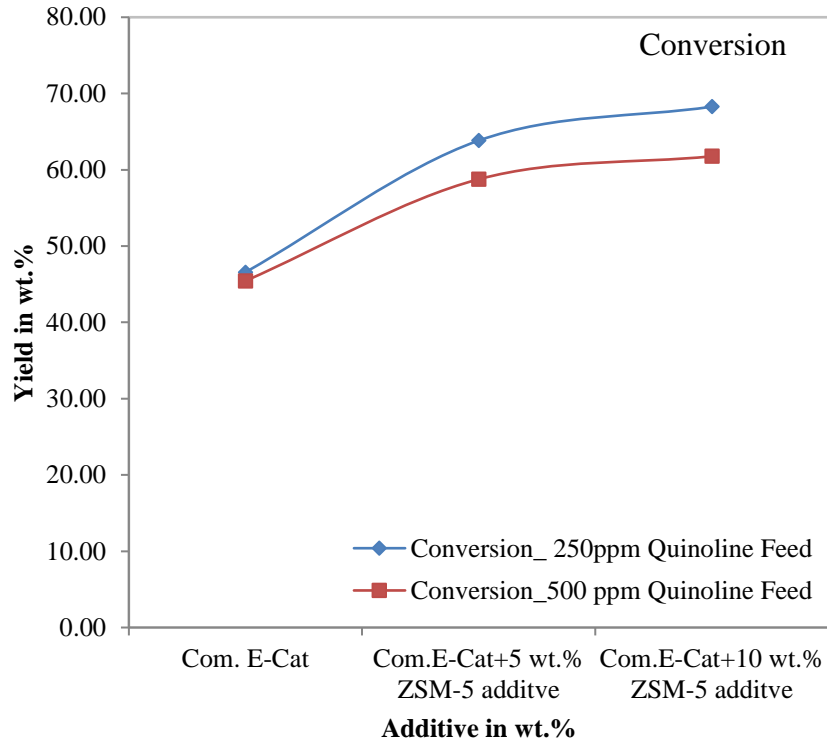Fig 4.2.2.5 Effect of ZSM-5 additive on Bottoms for Quinoline rich feed

Fig 4.2.2.6 Effect of ZSM-5 additive on Conversion for Quinoline rich feed

The effect of additive i.e. ZSM-5 on the quinoline rich feed is plotted and it is so concluded that the addition of ZSM-5 has a positive effect on the catalytic activity.

The conversion of quinoline rich feeds is increased by around by 20%. It is a postive effect on catalytic activity.

In this study, it is observed that the LPG is increased and gasoline is decreased; however the activity is increased due to the decrease of bottoms.

4.2.3 Effect of ZSM-5 on high nitrogenous feed

In this study, no model compounds are added to the feed and original high nitrogenous feed is used.

Base case analysis is done as a part of the study and those results are compared with the catalytic activity when ZSM-5 is added. The results are tabulated as below:

The feed characteristics and the experimental conditions are as follows:

Feed	VGO
Feed total nitrogen	1200 ppm
Cat/Oil	3.66
Reaction Temp.	510°C
Additive	ZSM-5

Table 4.2.3 Effect of ZSM-5 on Yield pattern and conversion

Product yield in wt.%	Com. E-CAT	Com. E-Cat+ 5 wt. % ZSM-5	Com. E-Cat+ 10 wt. % ZSM-5
H_2	0.22	0.17	0.19
Dry gas	2.35	4.04	4.56
LPG	19.82	27.59	31.16
Gasoline	43.35	38.37	36.73
LCO	19.73	15.85	14.09
Bottoms	10.76	10.26	9.58
coke	3.78	3.73	3.69
conversion	69.52	73.89	76.32
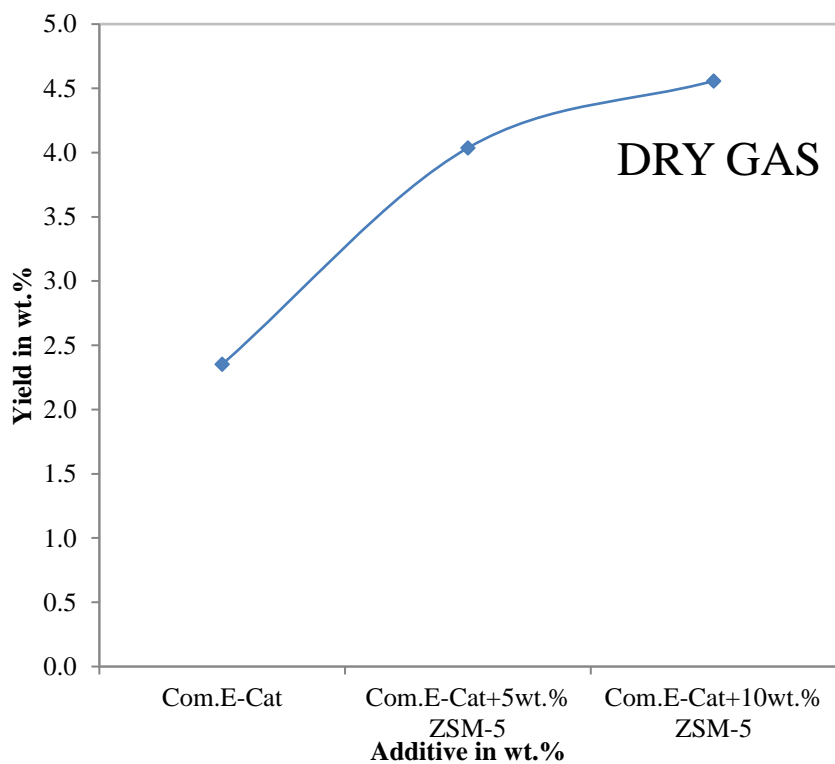
Fig 4.2.3.1 Effect of ZSM-5 on Dry Gas Yield
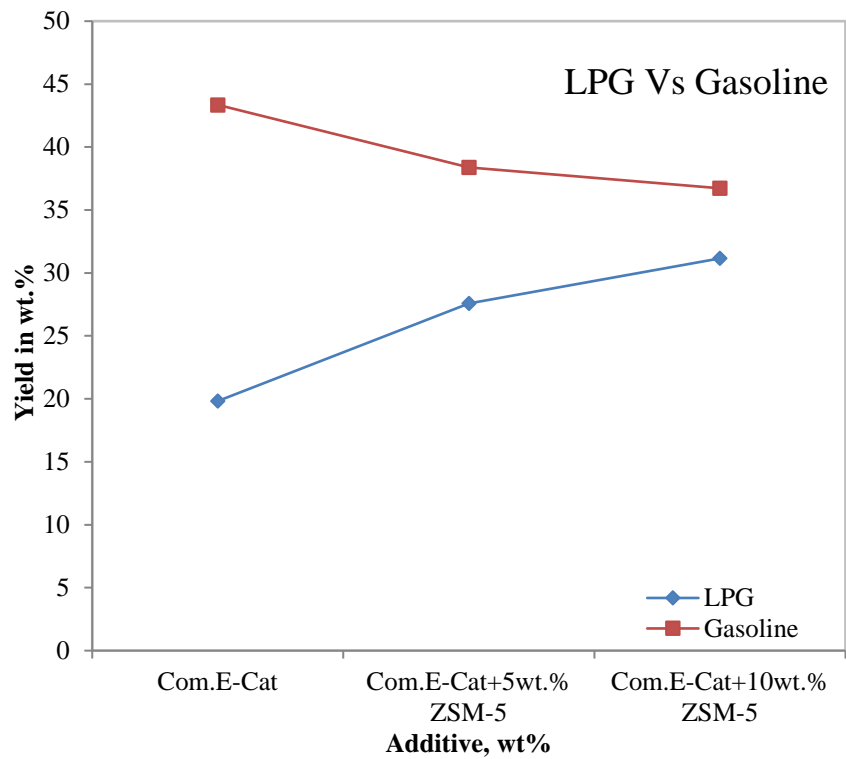
Fig 4.2.3.2 Effect of ZSM-5 on LPG and Gasoline yield
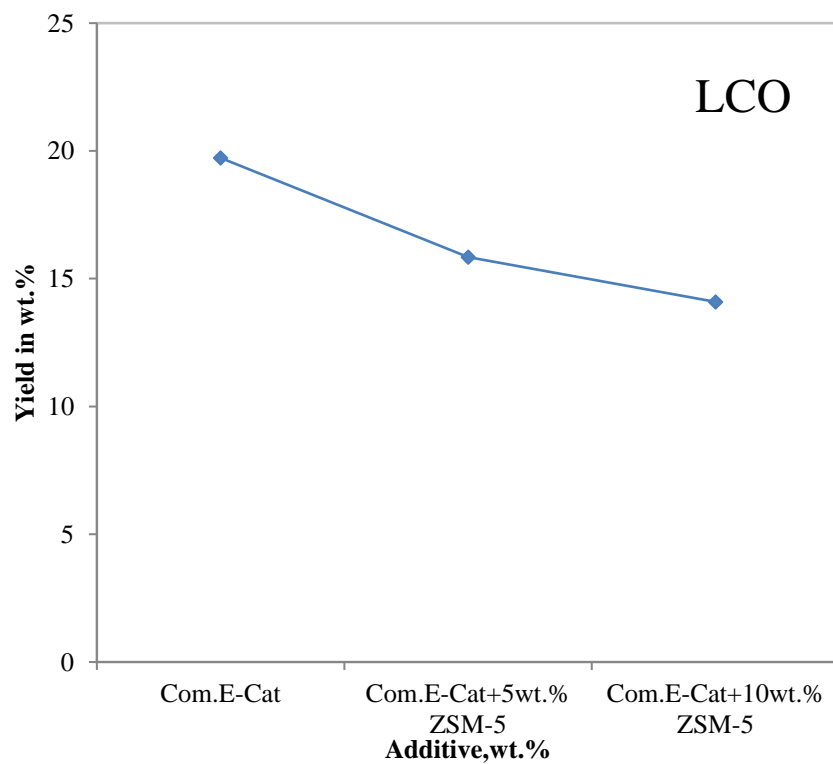
Fig 4.3.3.3 Effect of ZSM-5 on LCO Yield
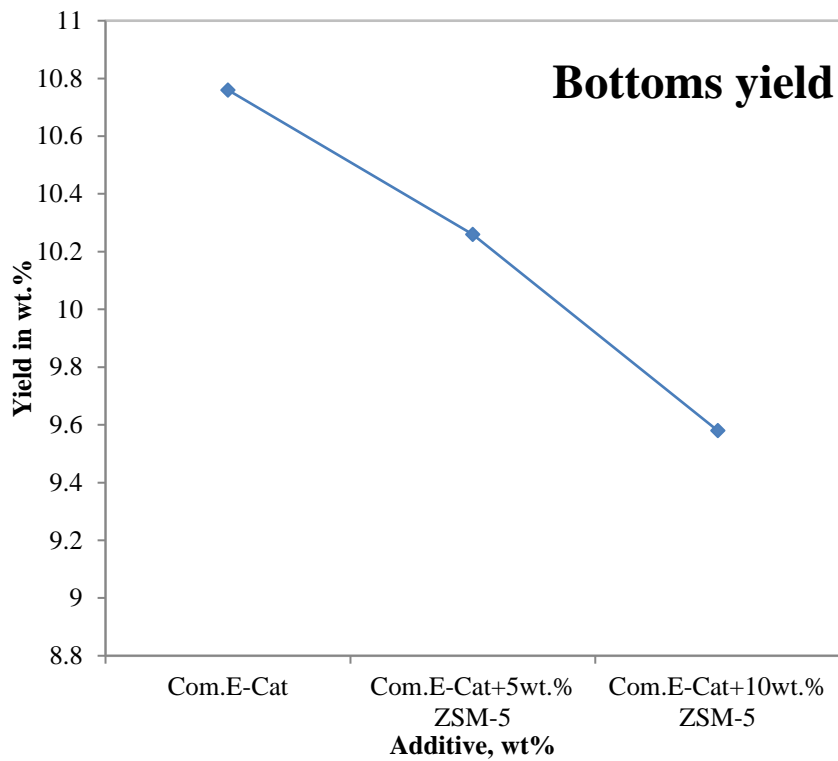
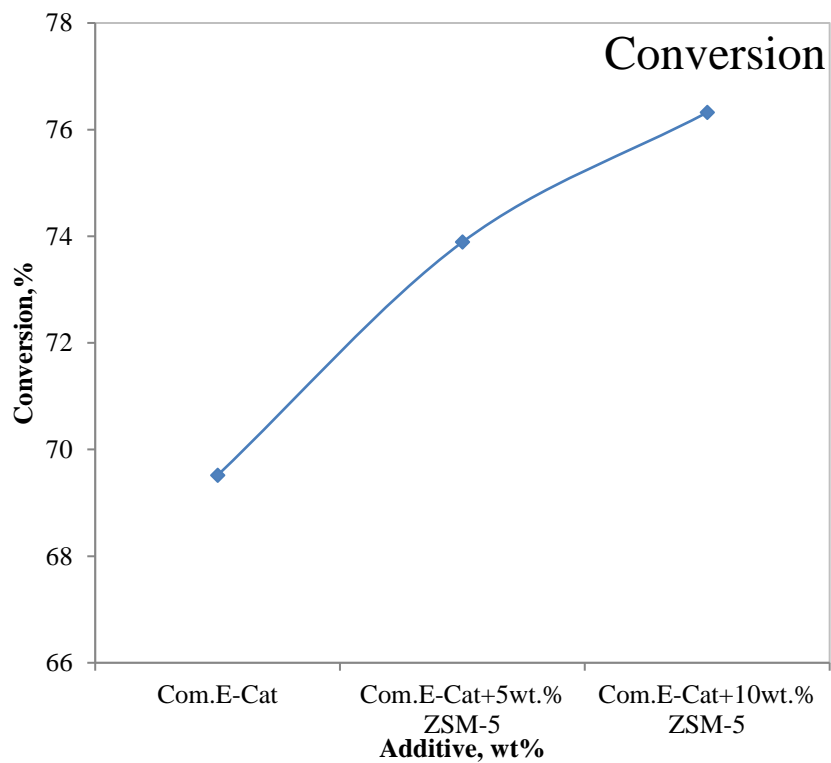Fig 4.3.3.4 Effect of ZSM-5 on Bottoms Yield

Fig 4.3.3.5 Effect of ZSM-5 on Conversion

By the addition of 10 wt. % ZSM-5, the conversion had almost increased by about 7 wt. %. There is a trend observed in the yield pattern of the products. The LPG composition had almost increased by about 15% by weight and there is drop observed in the gasoline pool.

The catalytic activity is increased but at the cost of the gasoline. These results are in accordance with the literature that the ZSM-5 additive is used for boosting the propylene.

It is therefore concluded that ZSM-5 is used in LPG Maximization mode of operation of FCC Process.

4.2.4 Effect of Bottom Cracking Additive (BCA)

As a part of study, the effect of Bottom Cracking Additive (BCA) is added in different weight percentages (5 wt. %, 10 wt. %). The additive is physically added to the catalyst and mixed well for uniformity.

The feed characteristics and the experimental conditions are as following

Feed	**VGO**
Feed total nitrogen	**1200**
Cat/Oil	**3.46**
Reaction Temp.	**510˚C**

The results are tabulated and the graphs are plotted for the yield and conversion.

Table 4.2.4 Effect of BCA on yield pattern and conversion

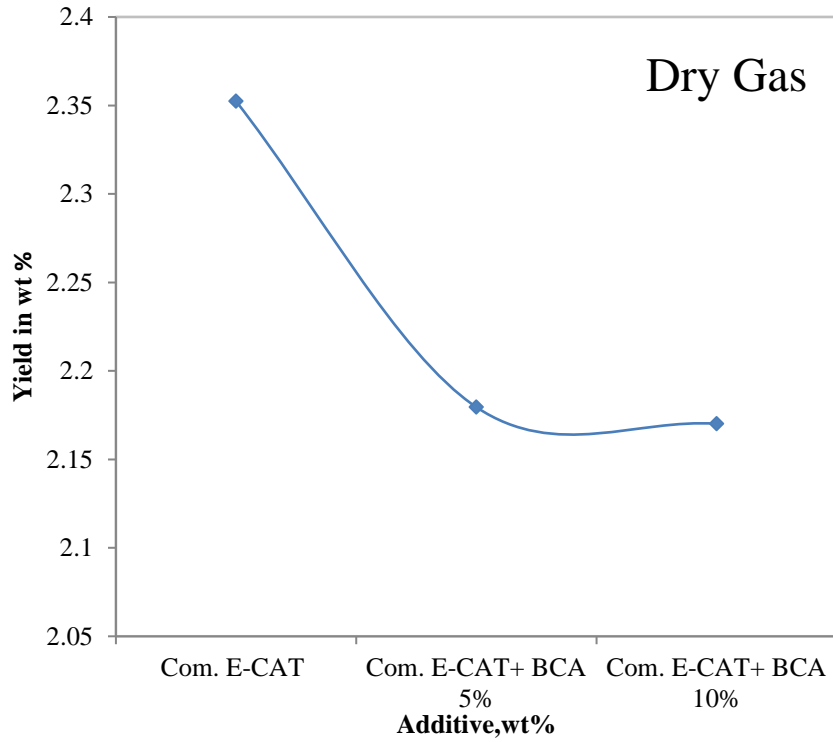| Product Yield, in wt.%	Com. E-CAT	Com. E-CAT+ 5 wt.% BCA	Com. E-CAT+ 10 wt. % BCA
H2	0.22	0.23	0.23
Dry gas	2.35	2.18	2.17
LPG	19.82	20.03	20.57
Gasoline	43.35	45.73	46.80
LCO	19.73	19.58	17.68
Bottoms	10.76	7.79	7.18
coke	3.78	4.49	5.45
Conversion	69.52	72.66	75.22

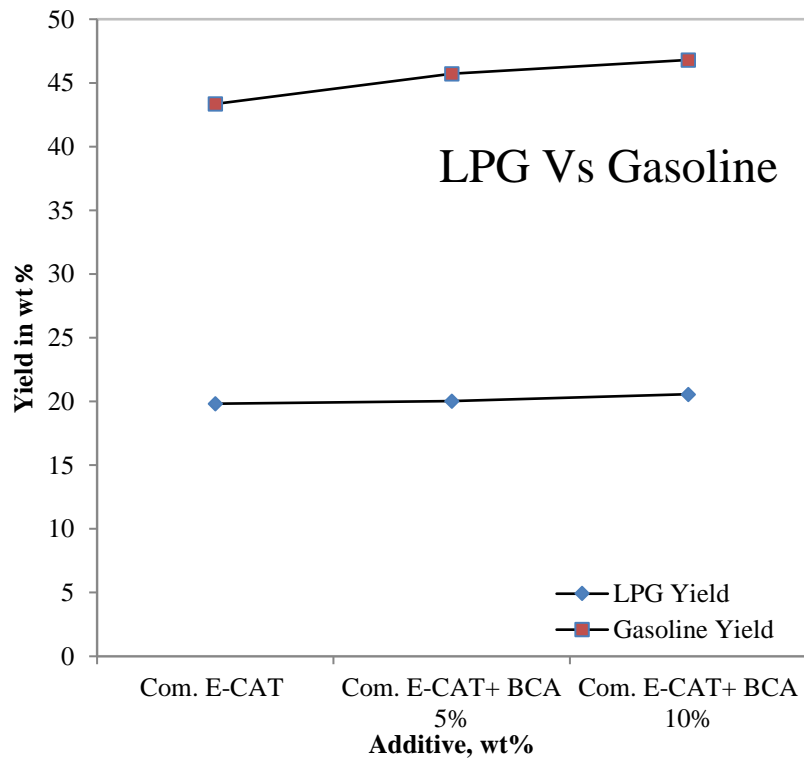Fig 4.2.4.1 Effect of BCA on Dry gas Yield

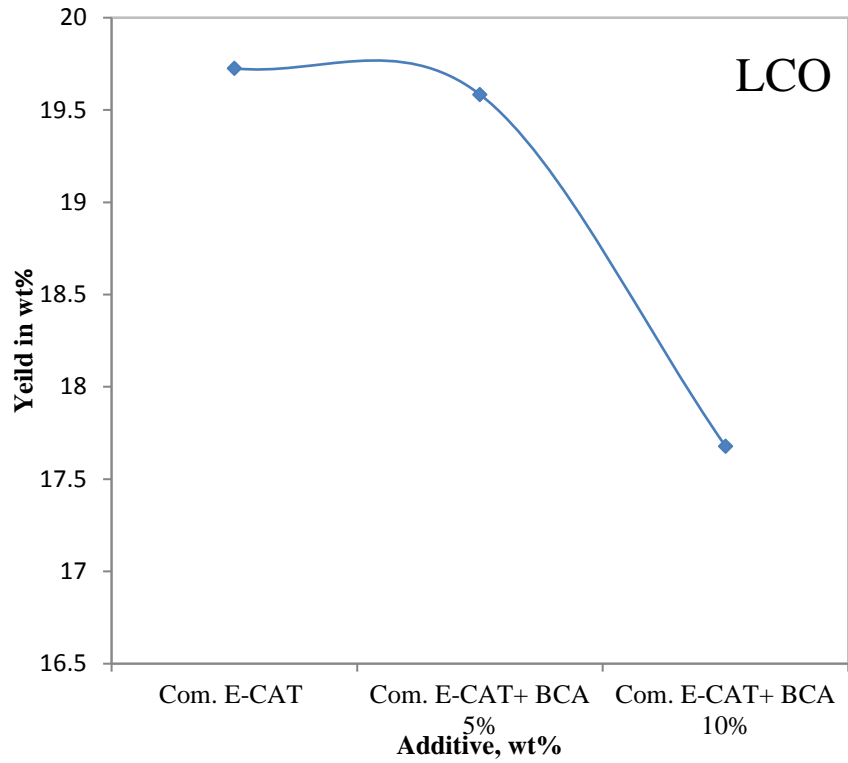Fig 4.2.4.2 Effect of BCA on LPG and Gasoline Yield
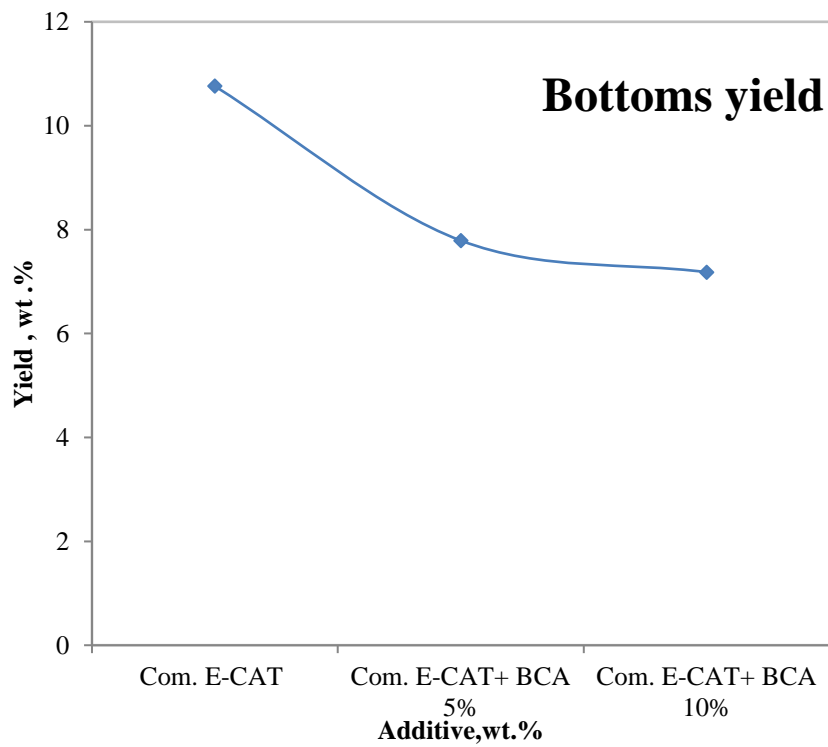
Fig 4.2.4.3 Effect of BCA on LCOYield
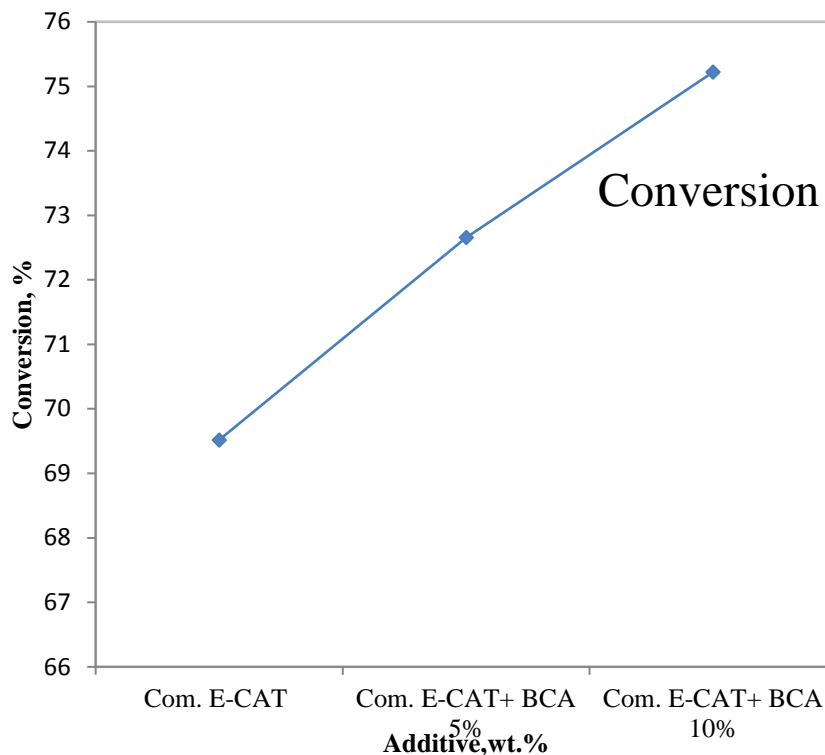

Fig 4.2.4.4 Effect of BCA on Bottoms Yield

Fig 4.2.4.5 Effect of BCA on Conversion

This study concludes that the activity of the catalyst is increased by 6wt. % without compromising the gasoline yields. In this study the composition of gasoline is retained and increased, there is also slight increase in the LPG yields.

4.2.5 Combined Additive Effect

As a part of study, the experiments are done such that both the additives are added to the base catalyst and the tests are carried out.

The studies are done for 5 wt. % total additive and 10 wt. % total additive. In addition, different ratios of both additives are tested and results are tabulated.

The feed characteristics and the experimental conditions are as shown below:

Feed	**VGO**
Feed total nitrogen	**1200**
Cat/Oil	**3.46**
Reaction Temp.	**510˚C**
Additive	**ZSM-5+BCA**

Table 4.2.5.1 Combined additive effect of BCA and ZSM-5 (total additive 5 wt. %) on yield and conversion.

Product yield in wt. %	Com E-CAT	Com. E-CAT+ 5 wt. % additive (ZSM-5, 20% & BCA, 80%)	Com. E-CAT+ 5 wt. % additive (ZSM-5, 40% & BCA, 60%)
H_2	0.22	0.18	0.18
Dry gas	2.35	3.88	3.96
LPG	19.82	22.16	24.97
Gasoline	43.35	42.30	40.95
LCO	19.73	18.66	16.68
Bottoms	10.76	7.05	7.22
coke	3.78	5.80	5.32
Conversion	69.52	74.33	75.38
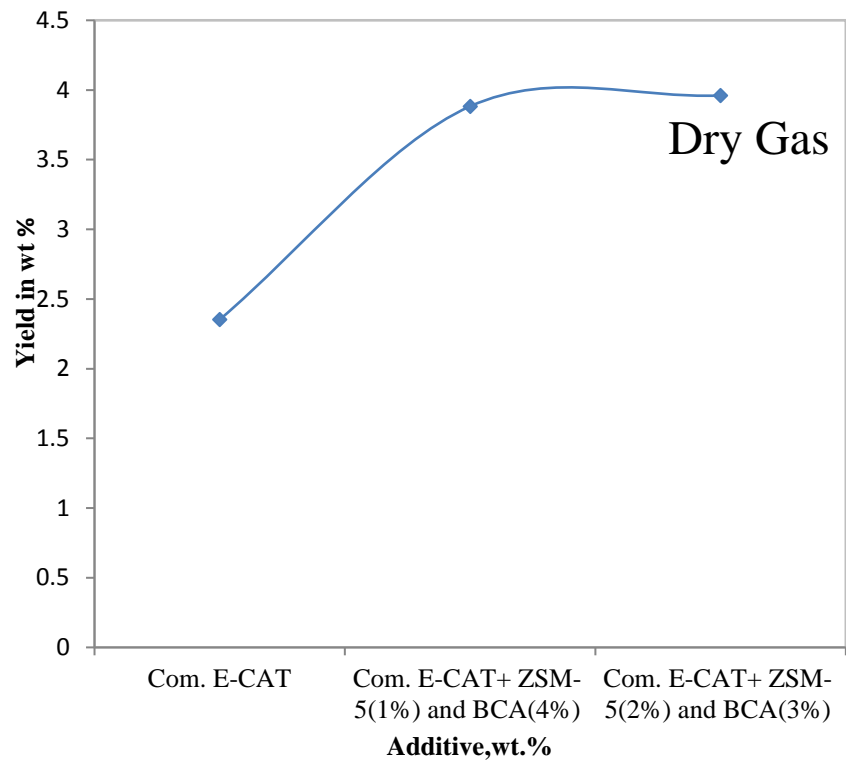
Fig 4.2.5.1 Combined additive effect of BCA and ZSM-5 (total additive 5 wt. %) on Dry gas Yield
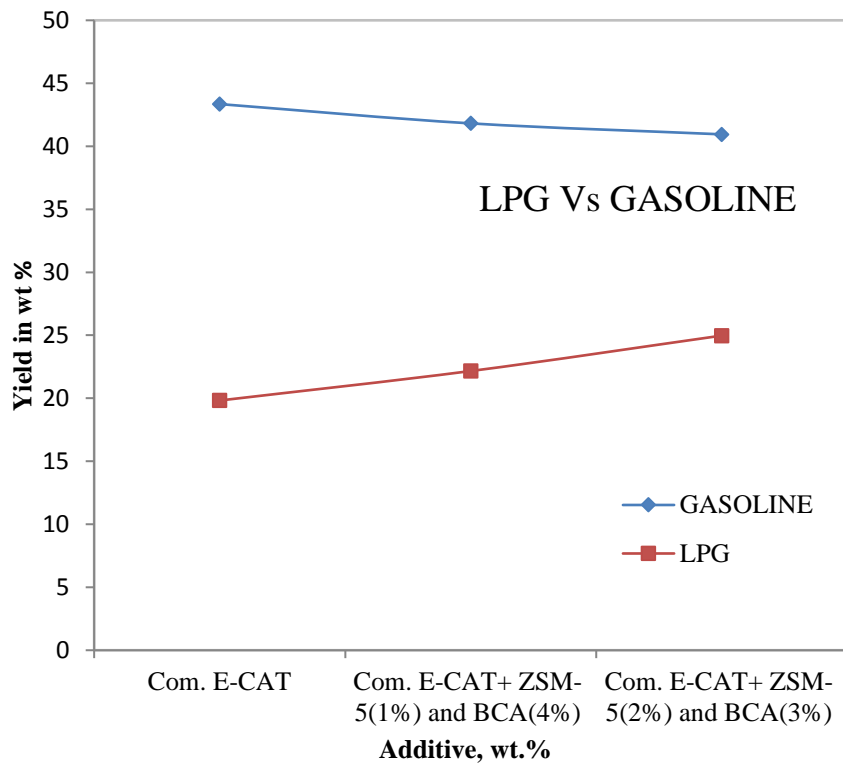
Fig 4.2.5.2 Combined additive effect of BCA and ZSM-5 (total additive 5 wt. %) on LPG and Gasoline Yield.
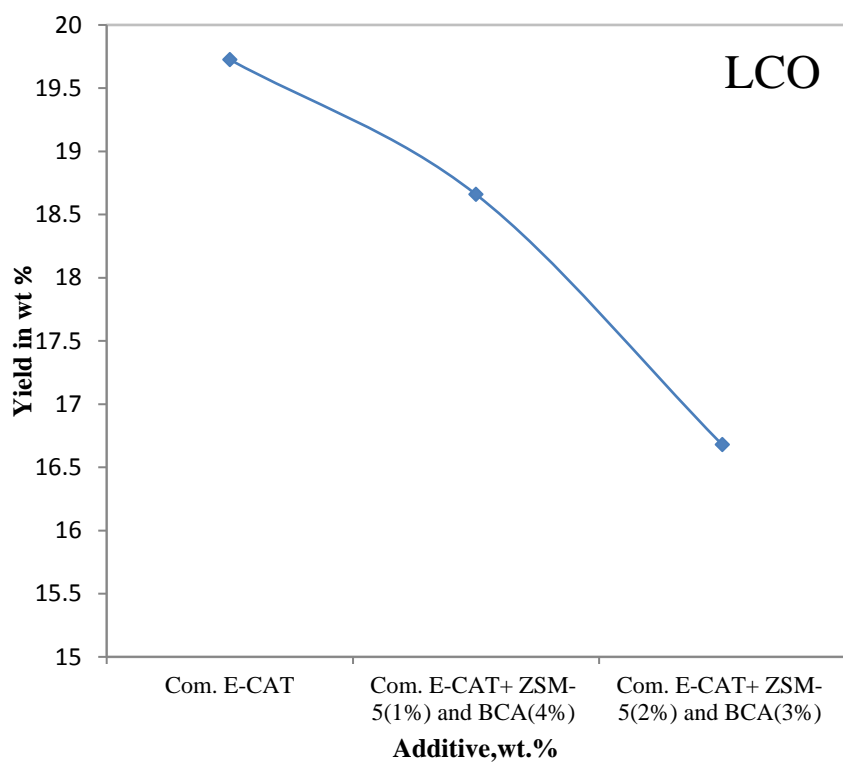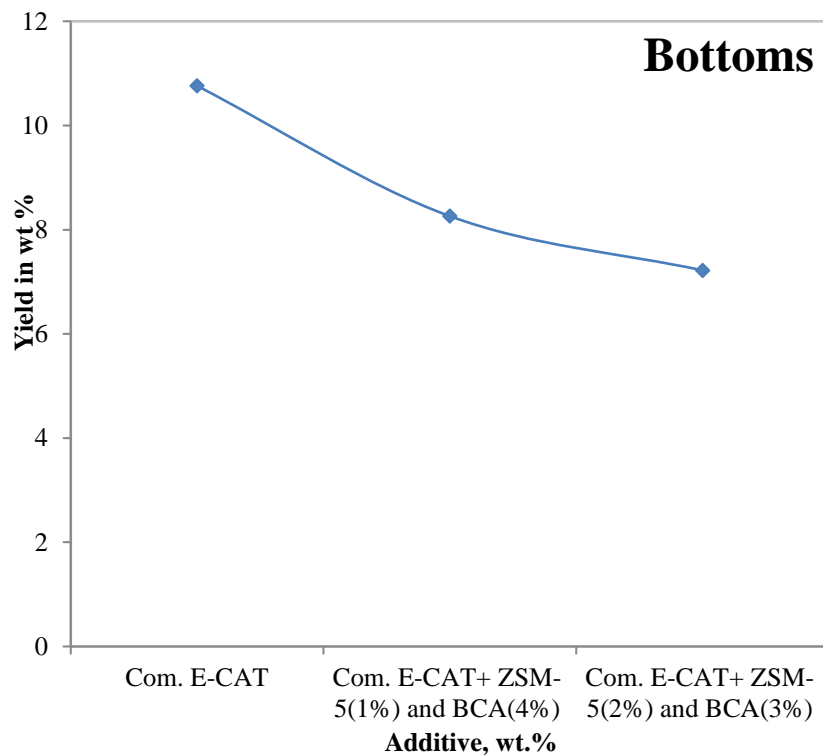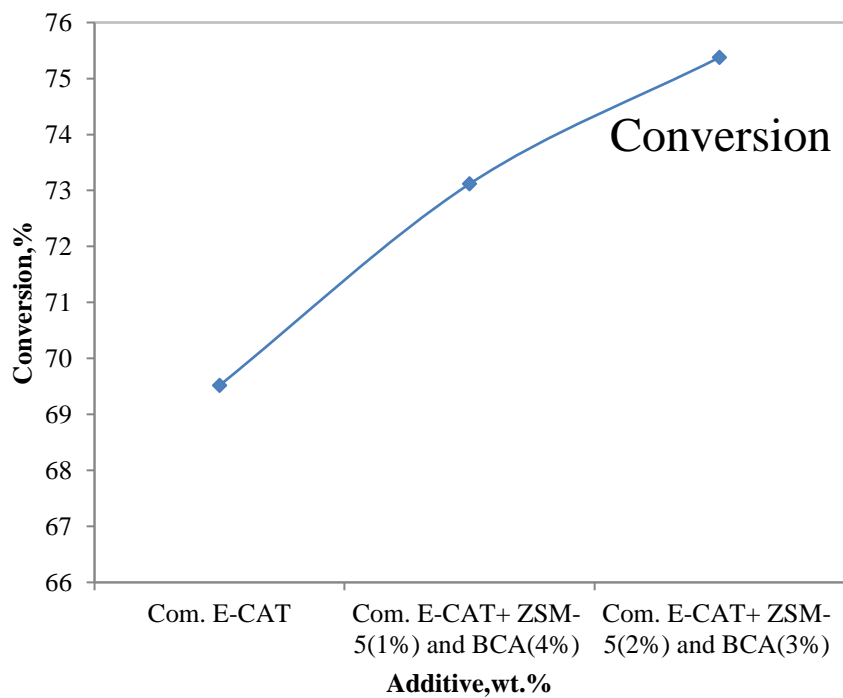

Fig 4.2.5.3 Combined additive effect of BCA and ZSM-5 (total additive 5 wt. %) on LCO Yield.

4.2.5.4 Combined additive effect of BCA and ZSM-5 (total additive 5 wt. %) on Bottoms Yield.

4.2.5.5 Combined additive effect of BCA and ZSM-5 (total additive 5 wt. %) on Conversion.

It is observed that the addition of 5 wt. % additive in different ratios of ZSM-5 and BCA had resulted in better catalytic activity than only BCA. It is also observed that the addition of ZSM-5 and BCA in (40+60) had resulted in increase of conversion by about 7%

The combined effect of additives for the total additive of 10 wt. % is also studied and the results are tabulated below. The feed characteristics and the experimental conditions are as follows

Feed	**VGO**
Feed total nitrogen	**1200**
Cat/Oil	**3.46**
Reaction Temp.	**510˚C**
Additive	**ZSM-5+BCA**

Table 4.2.5.2 Combined additive effect of ZSM -5 and BCA (total additive 10 wt. %) on yield and Conversion.

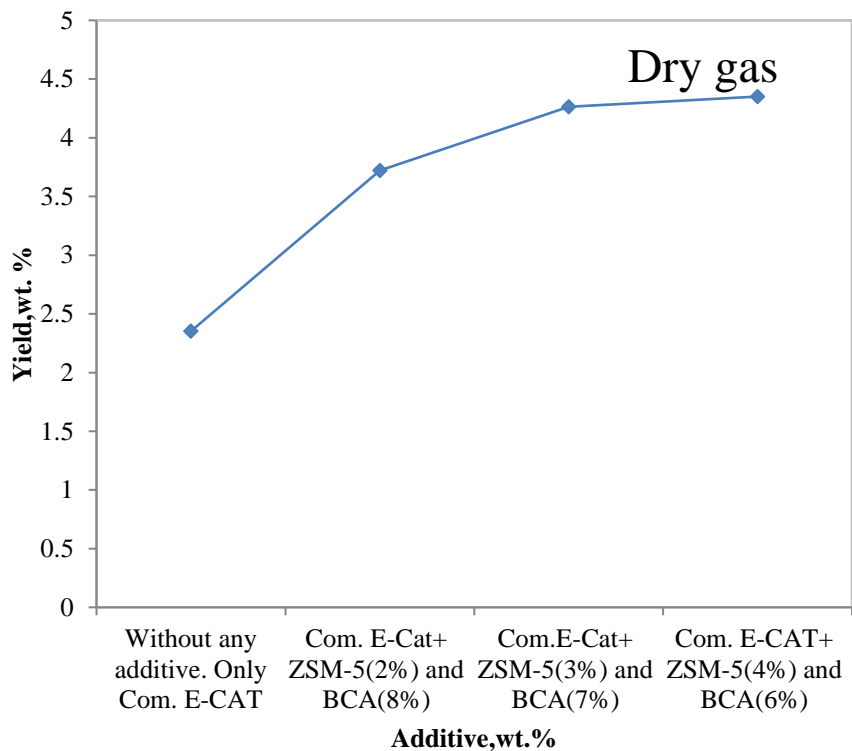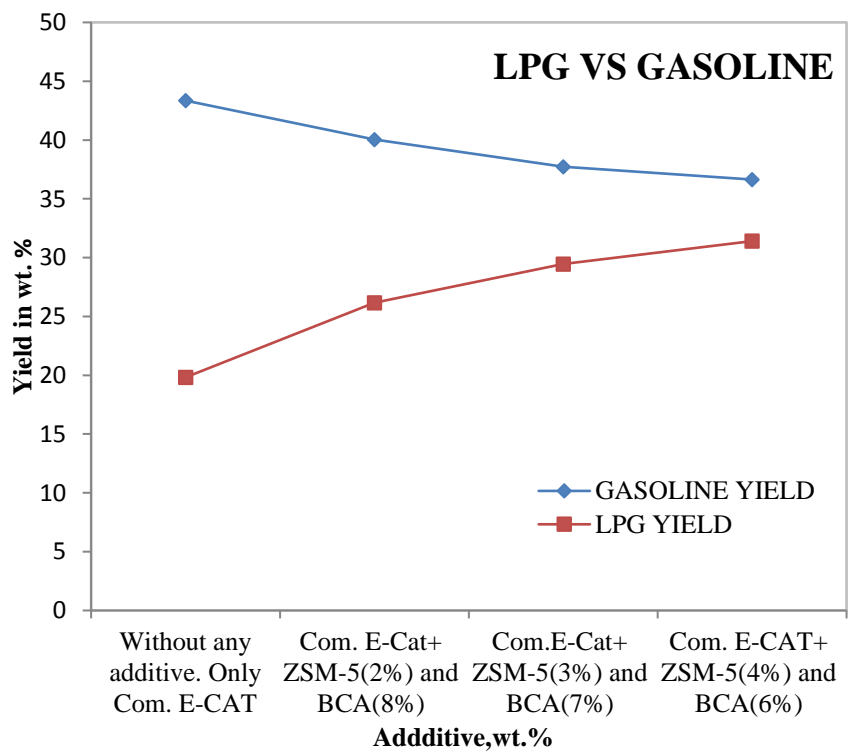| Composition	Com E-CAT	Com. E-CAT+ ZSM-5(2%) and BCA (8%)	Com E-CAT+ ZSM-5(3%) and BCA (7%)	Com. E-CAT+ ZSM-5(4%) and BCA (6%)
H2	0.22	0.19	0.13	0.20
Dry gas	2.35	3.72	4.26	4.35
LPG	19.82	26.17	29.46	31.40
Gasoline	43.35	40.90	37.72	36.64
LCO	19.73	16.46	15.91	15.24
Bottoms	10.76	7.05	7.28	7.04
coke	3.78	5.50	5.27	5.16
Conversion	69.52	76.48	76.84	77.75

Fig 4.2.5.6 Combined additive effect of ZSM -5 and BCA (total additive 10 wt. %) on Dry gas
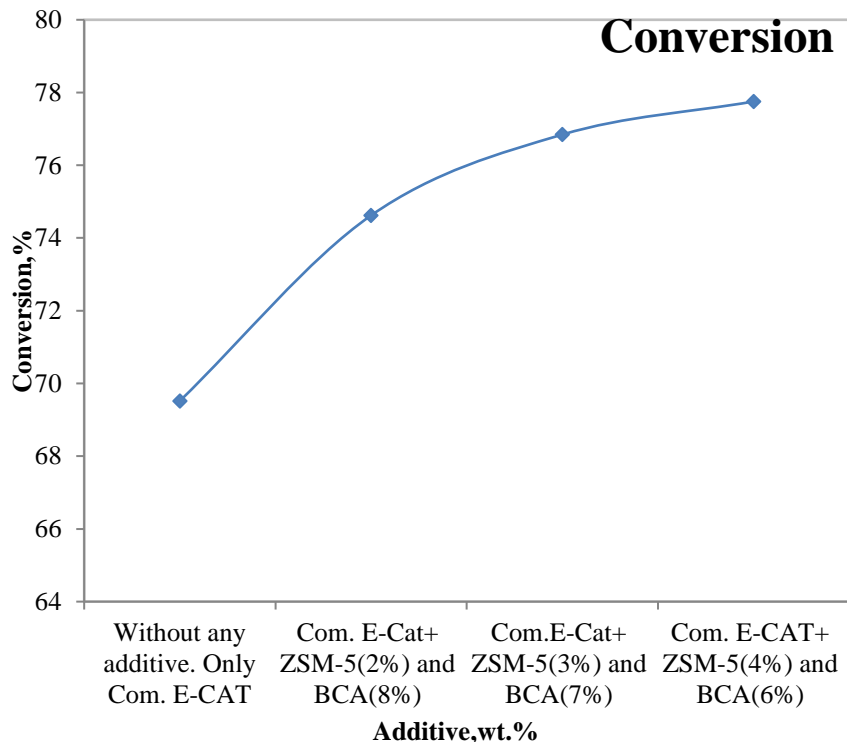

4.2.5.7 Combined additive effect of ZSM -5 and BCA (total additive 10 wt. %) on LPG and Gasoline yield
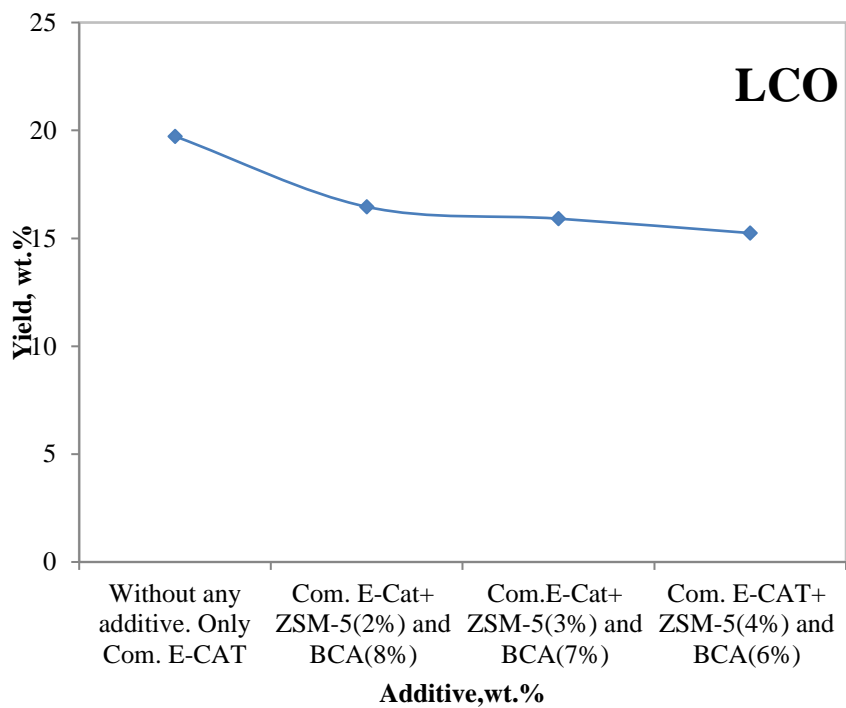
4.2.5.8 Combined additive effect of ZSM -5 and BCA (total additive 10 wt. %) on LCO yield
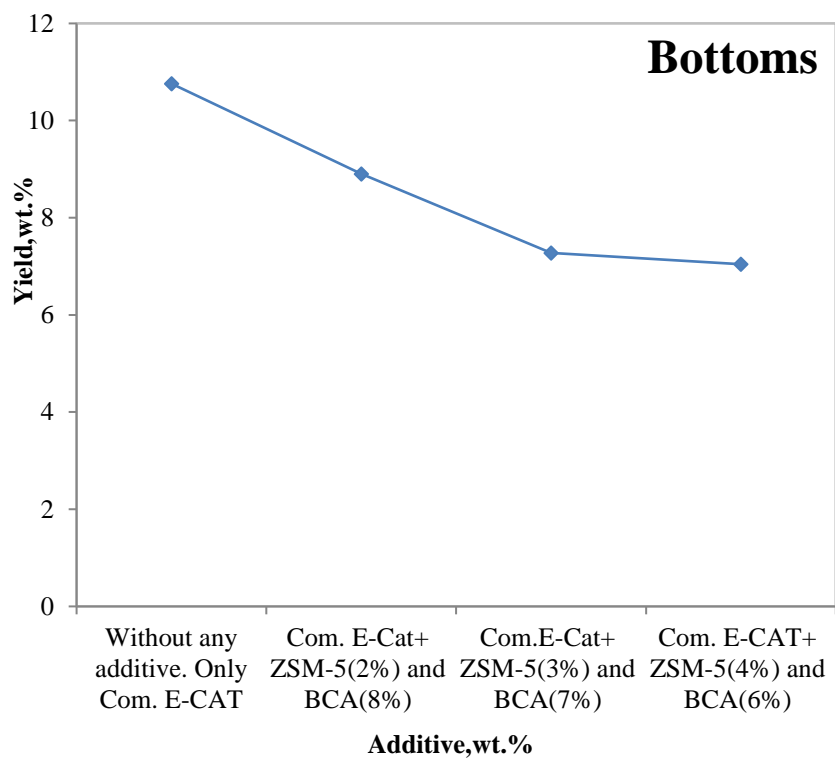
4.2.5.9 Combined additive effect of ZSM -5 and BCA (total additive 10 wt. %) on Bottoms yield

Conversion

4.2.5.10 Combined additive effect of ZSM -5 and BCA (total additive 10 wt. %) on Conversion.
In this study, the total additive is 10 wt. % and different ratios of two additives is used and the catalytic activity is increased.

The catalytic activity is increased as the LPG yield is increased, but the gasoline content is decreased. It is found that the 30% ZSM-5 and 70% BCA gives better and selectivity towards both LPG and Gasoline.

The catalytic activity is increased by around 8% with the use of 10% total additive in (40,60 combination).In this study it is observed that there is a decrease in LCO pool which contributes to the conversion

4.2.6 Effect of in-house formulated additives.

The high nitrogenous feed is cracked with in-house formulated catalyst additives. The experiments are carried out under the same conditions as in the previous runs and the coke studies are not done for these studies due to constraints. The feed characteristics and the experimental parameters are given below

Feed	**VGO**
Feed total nitrogen	**1200**
Cat/Oil	**3.46**
Reaction Temp.	**510˚C**
Additive	**BCA-18, BCA-19, BCA-20**

Table 4.2.6 Effect of in-house formulated additives on yield and conversion

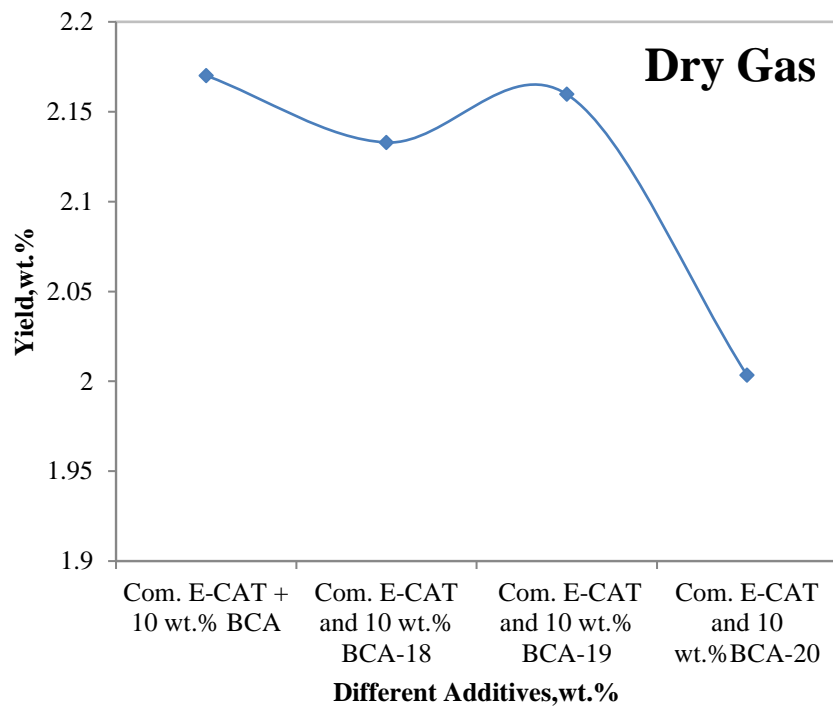| Product Yield in wt.%	Com. E-CAT + 10 wt.%BCA	Com. E-CAT and 10 wt.%BCA-18	Com.E-CAT and 10 wt.% BCA-19	Com. E-CAT and 10 wt.% BCA-20
H_2	0.23	0.22	0.21	0.27
Dry gas	2.17	2.13	2.16	2.00
LPG	20.57	21.65	22.68	18.81
Gasoline	46.80	48.60	49.77	51.35
LCO	17.68	15.69	14.49	15.37
Bottoms	7.18	5.75	6.45	5.72
coke	5.45	5.95	4.53	6.47
Conversion	75.22	78.56	79.35	78.91

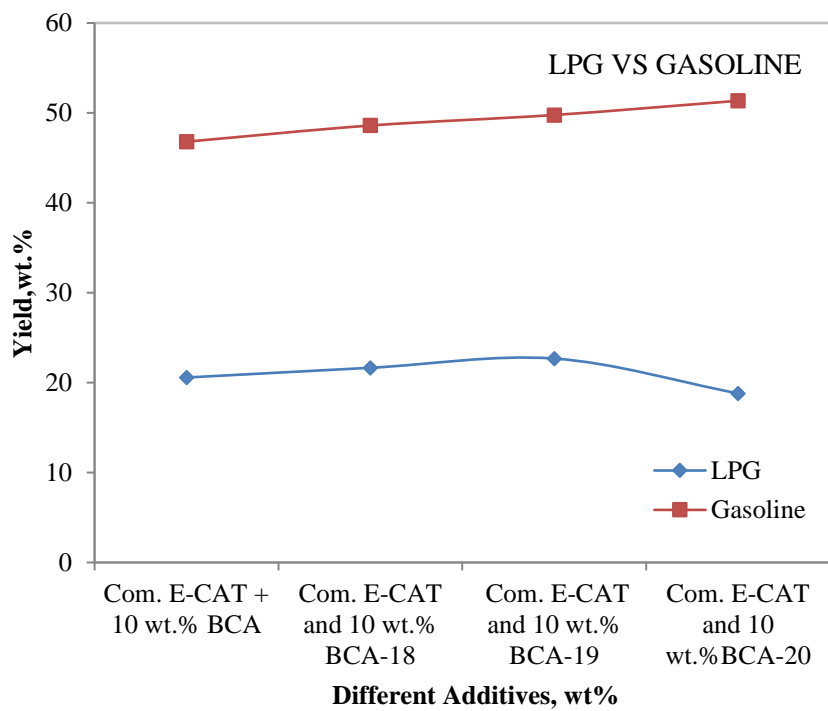Fig 4.2.6.1 Effect of in-house formulated additives on Dry gas yield

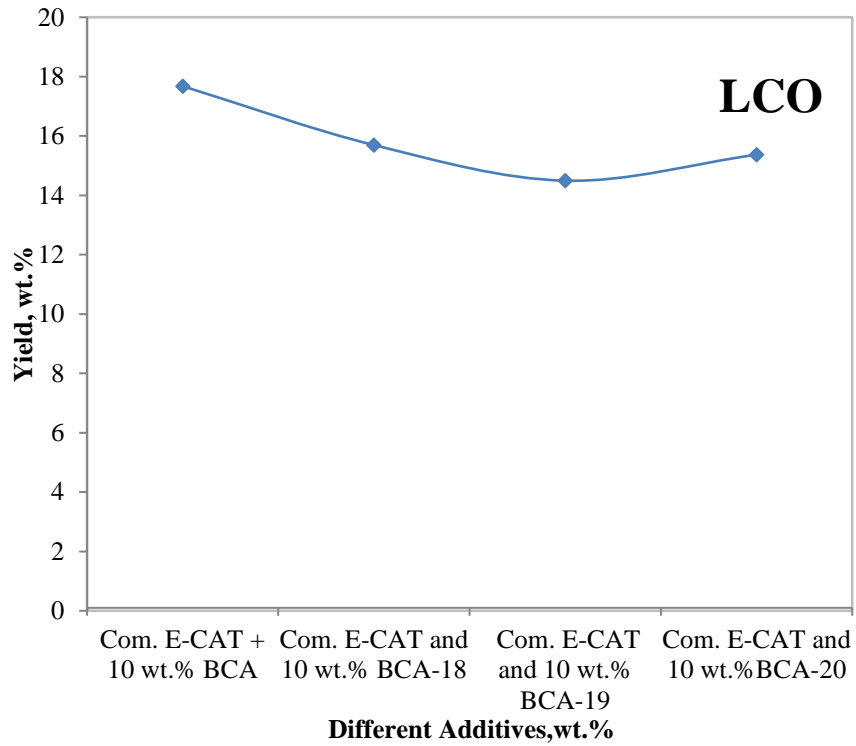Fig 4.2.6.2 Effect of in-house formulated additives on LPG and Gasoline yield

Fig 4.2.6.3 Effect of in-house formulated additives on LCO yield
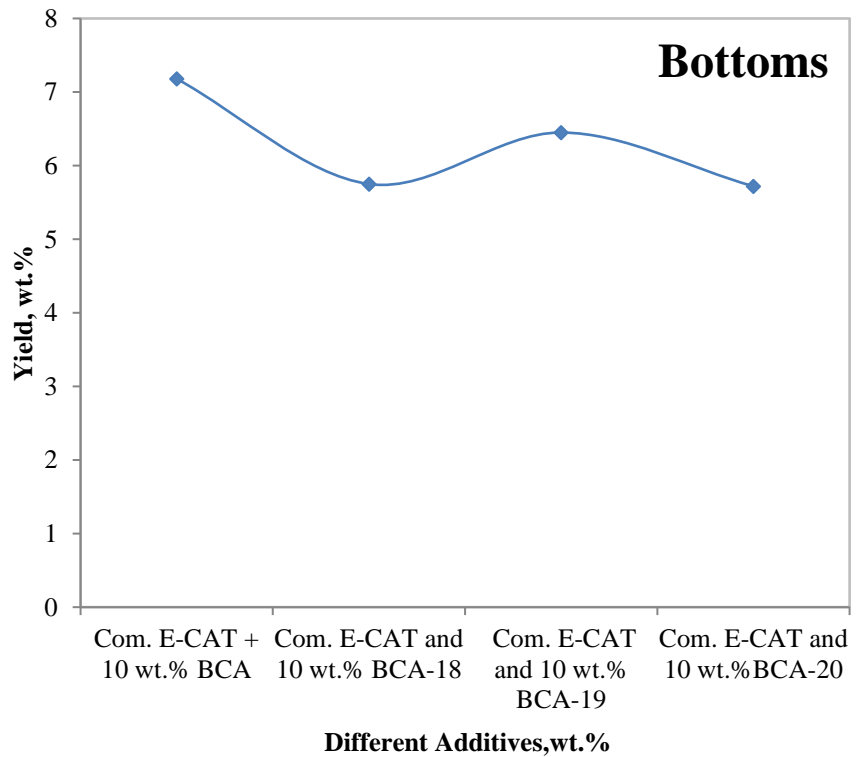

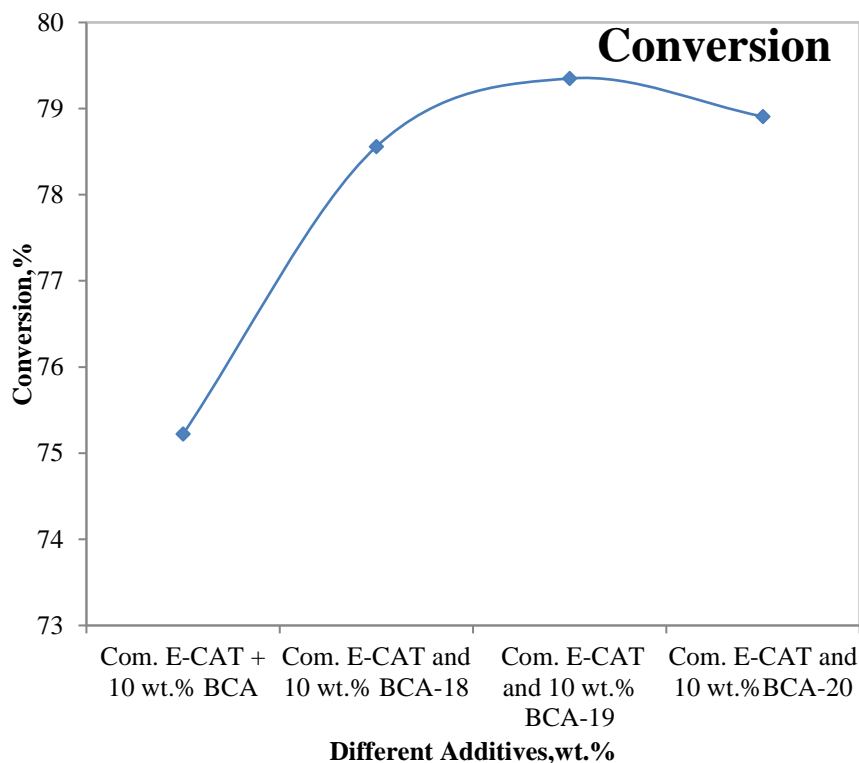Fig 4.2.6.4 Effect of in-house formulated additives on Bottoms yield

Fig 4.2.6.5 Effect of in-house formulated additives on Conversion.

The in-house formulated custom made catalyst additives are tested and for BCA-19 the overall conversion had increased by about 10% and when compared to conventional BCA, it had increased by 4% for the addition of 10 wt. % additive.

BCA-19 has low coke selectivity and high gasoline and LPG selectivity. The middle distillate pool selectivity is less for BCA-19 when compared to other additives. The bottoms and dry gas is more in the case of BCA-19, however the conversion is the highest.

BCA-18 has equal selectivities towards LPG, Gasoline and middle distillates. It showed medium coke and lesser drygas.The catalytic activity had enhanced by 9% overall and 3.3% compared to traditional BCA.

In case of BCA-20, the coke yields are higher and the overall conversion had increased by 9.3% and 4.6% increase is observed compared to conventional BCA.

This additive has higher selectivity towards gasoline and coke yields and slight decrease in LPG and dry gas is observed.

The middle distillate pool selectivity is also higher for BCA-20.

CHAPTER-5

CONCLUSIONS

As a part of study, it is concluded that the basic nitrogen compounds present in the feed, results in negatively impacting the catalytic activity.

Out of the two studied basic nitrogen compounds, quinoline is found to impact more to the catalytic activity because of bulky molecule and its higher proton affinity.

ZSM-5 can be used as additive (nitrogen scavenger) while processing high Nitrogenous feeds.

It is concluded from the studies on additives that the addition of ZSM-5 has a positive impact on conversion by contributing into the LPG selectivity. This conclusion is consistent with the previous works which have been done.

The other additive BCA which was tested also increased the catalytic activity by up grading the bottoms and by contributing into the middle distillate pools.

The addition of 5 wt. % total additive (ZSM-5+BCA) in 40:60 ratios gives the best yield, selectivity and conversion as compared to 10 wt. % addition of ZSM-5 and BCA separately.

The combined additive effect of ZSM-5 and BCA for 10 wt. % addition had increased the conversion by around 8% for (4% ZSM-5 and 6% BCA). However, the conversion achieved is at the cost of gasoline due to the presence of ZSM-5.

Out of the three additives tested, BCA-19 had given more conversion and has higher coke selectivity with higher yields of LPG and Gasoline.

CHAPTER 6
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