Preparation of ZSM-5 additive, characterization, performance evaluation and prediction of results under actual plant (FCC) conditions

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A thesis submitted in partial fulfilment of the requirements for the Degree of
Master of Technology
(Refining & Petrochemical Engineering)

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CERTIFICATE

This is to certify that **Mr. Kamlesh Upneja, a M.Tech (Refining & Petrochemical), 4th semester student from UPES, Dehradun** has undergone Internship/Industrial Training at **Indian Oil Corporation Limited, R&D Centre, Faridabad from 13.04.2009 to 22.05.2009.**

He worked on the project **"Preparation of ZSM-5 additive, characterization, performance evaluation and prediction of results in actual plant (FCC Unit) condition"** in Refining Technology I Department of R&D Centre.

He was found quite sincere and hard working during the training period.

I wish him all the success in future career.

25/5/09
(Dr. A. K. Gupta)
Chief Manager (TRG & CC)

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ABSTRACT

Fluidized Catalytic cracking unit is the main workhorse of any refinery as it decides the profit margin of the refinery.FCCU is capable to maximize any product which no other unit in a modern refinery is capable to achieve. This is done by either selecting the severity conditions or by employing different catalyst formulations.

Catalyst additive formulations have particularly been used in Fluid Catalytic Cracking application to carry out the product selectivity since 1980s.ZSM-5 additive is particularly used to maximize propylene which is of great economical value in the petrochemical industry. The additive activity can be further enhanced by taking different formulations to minimize the heavier and maximize the olefins content.

Continuous laboratory formulations are tried out to achieve the best formulations according to particular type of crude and refinery conditions. These lab prepared are tested for their performance and yield pattern by pilot plant studies or MAT study. However MAT test has significantly gained wide importance due to its near to actual conditions and product pattern.

At IOC R&D centre,I have prepared one such ZSM-5 additive characterized and tested the performance under MAT study to predict the performance of the catalyst with the commercially available catalyst formulations.

Chapter 1

INTRODUCTION

1.0 Introduction

Crude oil is the dominant energy source in the world economy .The direct distillate of crude oil does not provide sufficient amount of light hydrocarbon fractions in order to justify various downstream operations in order to adapt to products offered to the markets demand as well as product specification.

The fluidized Catalytic Cracking (FCC) is an important refinery process (reference 2) used for the conversion of heavy petroleum fractions to lighter and valuable products. In FCC, zeolite based catalyst micro spheres, in the size range of 20-120 microns, are continuously circulated between reactor and regenerator vessels. In the riser-reactor, the feed vapors are brought into contact with fluidized catalyst resulting in catalytic cracking of hydrocarbons. The product hydrocarbon vapors enter the main fractionators and followed by gas concentration unit, where all products like dry gas, LPG, gasoline, diesel get separated. The spent catalyst after the stripper enters into the regenerator. In regenerator, the coke deposited on the spent catalyst is burnt off in the presence of air at temperature of 650-730 degrees centigrade. Cracking reactions are endothermic in nature and the energy requirement is met by the heat generated in the regenerator due to coke burning. The heat produced in the regenerator is supplied to the reactor via continuous catalyst circulation. Here catalyst acts as a heat carrier. Thus, there exists a critical heat balance in FCC unit, which significantly influences most of the dependent process variables like product yields, operating temperatures etc.

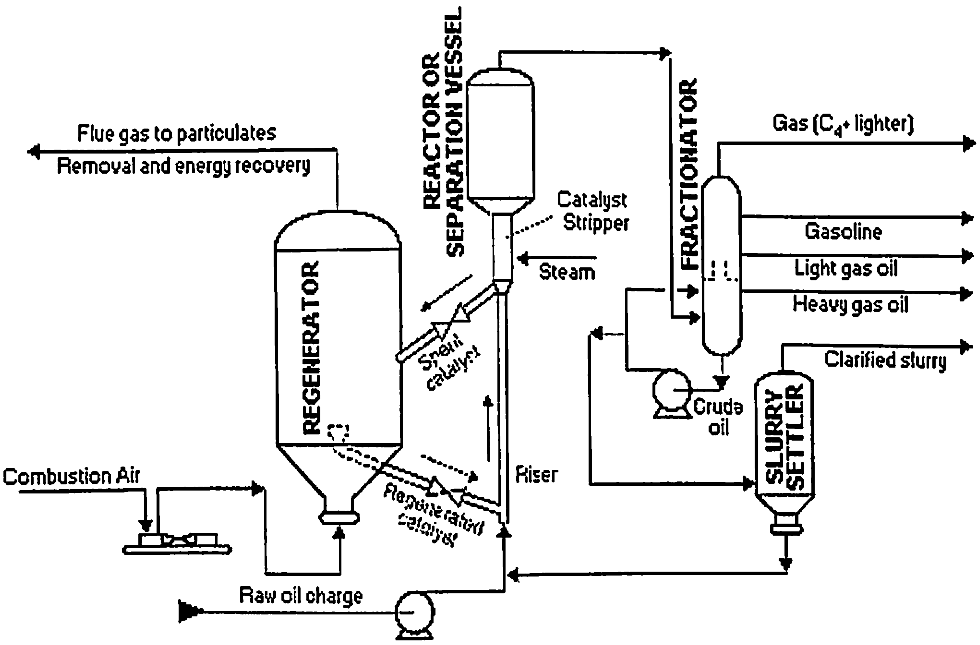


Figure 1.1 Schematic diagram of Fluid Catalytic Cracking Unit

Till date one of the major refining operation, FCC is responsible for the conversion of heavy feed distillates (gas oils from vacuum distillation tower or residues from atmospheric distillation tower) into lighter, more valuable products such as liquefied petroleum gases (LPG) and gasoline. Besides the decline in cracking reactivity, coke formation also occurs in these systems. This coke temporarily deactivates the active sites of the catalyst by poisoning or preventing diffusion of molecules mainly through small pores resulting in an important activity loss. In order to recover the activity, the FCC catalyst continuously circulates between the riser (FCC reactor) and the regenerator. In the regenerator, the coke is converted into CO, CO_2, H_2O, Sox and Nox compounds.

Depending on the crude oil source, the FCC feedstock may present different amounts of contaminant metals. The most common are vanadium, nickel, sodium and iron. These metal act as poison to the zeolite (the key component of the cracking catalyst)acid sites and present dehydrogenating characteristics.

In order to cope with the losses due to catalyst attrition and maintain catalyst activity(reference 1), fresh catalyst makeup is frequently needed. For some FCC units, process feedstock with high level of metals, it is also frequent to withdraw a portion of the inventory in addition to the usual catalyst makeup to accelerate the replacement of catalyst by fresh portions and keep contaminant metals at an acceptable level. The fresh catalyst addition needed to maintain the activity of the inventory (1400t/day) for 300 FCC units worldwide make the FCC process the most important catalyst market.

Since petrochemical integration along with refinery (mainly propylene maximization) is an important consideration these days, hence FCCU is generally looked as important source for petrochemical feedstock for improving the profitability.

Generally two options are in use for increasing propylene yield in FCC unit, viz. operational and catalytic. Operational option includes increasing reactor temperature, conversion and using more paraffin feed. However this option is not easily controllable to obtain the desired propylene yield. Hence most preferred option is use of catalyst. The use of variety of specific purpose additives has significantly improved the flexibility and operation of FCC units over the years. Without any hardware change, the catalyst additive approach allows FCC units to accommodate variety of operational needs. ZSM-5 additives or catalysts increases LPG especially propylene in the FCC unit by cracking gasoline range hydrocarbons.

Although FCC is a process that has been commercially deployed for over 60 years, the technology continues to evolve to meet new challenges, which include processing more difficult feedstock and meeting more stringent environmental regulations. Modern FCC units can process a wide variety of feedstock and can adjust operating conditions to maximize production of gasoline, middle distillate olefins (LCO) or light olefins to meet different market demands. FCC is the most important industrial application of zeolites.Carried out using zeolite Y. High molecular weight hydrocarbons are broken down into lighter fragments. This cracking process is an acid catalyzed carbenium ion rearrangement .Zeolite inhibits formation of coke etc

For overcoming limitation in FCC catalyst in producing LPG yield beyond certain limit, additive catalyst(reference 3e) made with ZSM-5 zeolite has been in practice for the last two decades. These additive were available initially with zeolite content of 10 wt %.Due to higher expectations from the refiners to produce higher LPG yield, manufacturers have been producing these additives at 25 wt % zeolite content. However performance analysis shows that higher ZSM-5 content in additive necessarily need not produce higher LPG.This needs thorough understanding of binder, zeolite, catalyst slurry composition, slurry properties and process conditions and their effect on the performance of the catalyst.

ZSM-5 was first introduced into the fluid catalytic process as an additive for improving gasoline octane in the early 1980's. However, it is now primarily used to increase the yield of C3 and C4 olefin for alkylation, oligomerisation and other petrochemical processes. The current primary role of fluid catalytic cracking as a gasoline fuel producer is shifting towards being a producer of light olefins in many refineries. It is generally agreed that ZSM-5 cracks the gasoline range olefins or olefinic precursors into light olefins including C3, C4 and C5 olefins. FCC gasoline composition typically shows lower paraffin with the presence of ZSM-5.It is due to reduced levels of olefinic precursors to paraffin's rather than direct cracking of paraffin by ZSM-5.

Almost the decade passed between the initial discovery of ZSM-5 in 1965 and its initial commercial trial in 1982. The motivation of developing a ZSM-5 additive changed over the course of its development. Beginning in the mid 1980s a need developed for 'cleaner gasoline 'depleted of sulfur, olefins and aromatics. This in turn produced favorable economics for light Para propylene alkylation. Finally in the early 1990's a robust market for polypropylene drove an interest in producing more propylene from FCC units. The stability of ZSM-5 was examined in the late 1960s.It was soon found that the highly siliceous nature and the structure of ZSM-5 provide both a very thermally and a very hydrothermal stable zeolite.The zeolite could be treated at temperatures as high as 1260 degree centigrade before encountering any deteoriation

ZSM-5 has found widespread application as a fluid catalytic cracking additive for both propylene production and gasoline octane improvement. Thus the decision to use this technology boils down to economic trade off between the value of gasoline and the value of LPG.

Propylene demand-supply scenario:

Propylene is a co-product of steam crackers where the primary product is ethylene along with polymer grade/chemical grade (PG/CG) propylene. FCC contributes around 30% of the total propylene supply as a by product along with it transportation fuels production.

In the Asia pacific region propylene supply is shifted more towards steam cracking (more specifically naphtha cracking which accounts for almost 75 % of the regional propylene supply) while only about 25 % is supplied from FCC units. The world shift in global supply of petrochemicals for mostly ethylene derivatives from the Middle East to Asia will increase the emphasis on the FCC unit as a critical source of propylene in the region.

It is estimated that during the next few years the petrochemical industry in Asia will experience a significant propylene supply deficit. Even after the expansion of steam cracker capacity will meet the demand for ethylene derivatives, propylene derivatives demand will however could not be met with the propylene supply. In addition LPG demand in the region will continue at the robust rate. LPG is important for domestic heating, cooking and transportation in Asia notably India and China.

The market for propylene as basic intermediate petrochemical continues to grow at an average rate of 4 to 5 % per year. The largest source of propylene supply to the petrochemical market is steam crackers followed by Fluid Catalytic Cracking unit (FCC).The performance optimization of FCC units is largely depended on selection of best suite catalytic additive.

In this report, I have prepared one such ZSM-5 additive, characterized fully for apparent bulk density, attrition index and surface area and finally evaluated the by micro activity test (MAT) unit to check its performance and obtain predicted yield from lab scale to plant scale.

Chapter 2

Literature Review

When ZSM-5 was first evaluated as a cracking catalyst in the Mobil laboratories, its initial evaluation was quite unremarkable. A blend of 10% rare earth exchanged zeolite Y (REY) and unsteamed 5% ZSM-5 evaluated in a fixed bed gave the same octane improvement as REY alone. However additional experiments showed that the heavier fraction of FCC gasoline (boiling above 355 k) could be separately upgraded over ZSM-5 and that octane did increase when this was blended back with the lighter gasoline.

Biswas and Maxwell(reference 5) examined the effect of adding ZSM-5 as a separate particle to a USY catalyst over a range of ZSM-5(crystal loading) ranging from 0-3 wt %.They showed that gasoline yield decreases in direct proportion to the amount of ZSM-5 that is added. Conversely they showed that butylenes and propylene increases at the same rate in proportion to the amount of ZSM-5 that is added.

In other study, which examined the effects of ZSM-5 used in combination with USY, Madon noted that doubling the ZSM-5 content (from 1.1 to 2.2 wt %) doubled the RON and MON increase but did not double the gasoline yield loss. He attributes this to changes in the reaction in the gasoline fraction with compositional changes produced by ZSM-5.

In FCC applications, ZSM-5 content has ranged up to 3 wt % (expressed as wt % of ZSM-5 crystal) of the total inventory. The targeted ZSM-5 loading is dictated not only by the desired octane increase or light olefin production levels, but also by the base octane, gasoline cut point, regenerator temperature and base catalyst make up rate.

Several of studies have examined the effect on gas oil cracking of adding fresh, calcined ZSM-5 to USY or REY FCC catalysts. There have conclusively shown paraffin selective cracking under FCC conidtions.For example Rajgopalan (reference 7) observed a selective 20% reduction in paraffin after adding 1 wt% of thermally treated ZSM-5 component (704 degrees in air for three hours) to a steamed REY catalyst in cracking commercial gas oil. The gasoline product was enriched in olefins and C6 to C8 aromatics. Paraffin conversion diminished when the ZSM-5 catalyst was severely steamed. in typical FCC operations, fresh catalyst is added to the regenerator. Therefore the catalyst always undergoes some degrees of hydrothermal deactivation (heat and steam water) deactivation before contacting the hydrocarbon feedstock. For this reason, the majorities of the studies aimed at elucidating the ZSM-5 mechanism in FCC and have used samples of ZSM-5 catalyst in which the zeolite has been placed in a conventional FCC matrix and then exposed to high temperature steam for a period of hours. The steamed catalyst have either been examined alone or physically combined with REY or USY based FCC catalysts.

Various steaming conditions have been used to simulate the equilibration of the additive under typical FCC regenerator conditions. Normally the additives are steamed at temperatures above 700 degrees for periods ranging from7 to 10 hours. Additive level typically 0.5 to 3 wt % ZSM-5 (as crystal) is added to simulate the commercial applications.

Furthermore, process condition in the FCC unit and feedstock will also affect catalyst performance. For any given catalyst formulation, the change of process parameters during catalytic cracking will change the resulting conversion and product yields for eg.conversion increase with reaction temperature or catalyst to oil ratio and decrease with increase in space velocity.

Chapter 3

ZEOLITE AS FCC CATALYSTS

Zeolite based FCC catalysts evolved directly from the amorphous catalysts used in the 1940's and 1950's.When first introduced in the 1960, zeolite cracking catalysts contained either type X or type Y incorporated in different matrix compositions. The main purpose of a matrix in the early zeolite catalysts was to moderate the high intrinsic activity of the zeolite to prevent its rapid deactivation as a result of coke formation.

Throughout the 1960's as well as 1970's zeolite containing FCC catalysts were modified to take advantage of the increased conversion and liquid yield and low coke afforded by catalytic cracking over zeolites. Today new demands are requiring FCC catalysts to increase the yields of light olefins and branched isomers in reformulated gasoline. Such demands require large range of catalyst compositions to meet different feed types.

During the 1970's and 1980's the "additive "era of the FCC catalysts evolved. Separate co-catalysts designed to control carbon monoxide and SOx emissions were commonly used. Nickel and vanadium passivators are also commonly used in high metals residual feed operations either as additives or as an integral part of the catalyst particles to increase the motor octane of gasoline, increase the total LPG or increase the olefin content of the fraction.

Conventional Y zeolites are used in FCC catalyst mostly in the form of rare earth, hydrogen (RE, HY) zeolites. The commercial rare earth salts are a mixture of lanthanum and cerium salts, with a smaller amount of neodymium and praseodymium. The presence of rare earth in the zeolite increases its stability and catalytic activity.

As such the Y zeolite imparts thermal stability but in order to further improve the stability, two alternative methods are adopted:

One is to exchange the sodium of zeolite with rare earth and the other is to dealumination zeolite under hydrothermal conditions. While the earth exchange increase the coke forming tendency of the catalyst, the dealumination leads to loss of zeolite crystalline and hence activity. Moreover the dealumination process to produce ultra stable Y zeolite is quite expensive. Since the dealuminated USY zeolite have significantly reduced coke forming tendency and they produce gasoline of higher octane number, they are replacing the rare earth exchanged zeolite in many catalyst formulations. In some cases to maintain a balance between good activity, low coke make and higher octane gasoline product, partially rare earth exchanged and dealuminated zeolite (RE USY) are used in some FCC catalysts. The improved stability is attributed to the formation of polynuclear, rare earth containing hydroxyl complexes in the zeolite sodalite cages. The improved activity is due to the higher number of Bronsted acid sites resulting from the partial hydrolysis of hydrated rare earth ions as indicated by the following reaction:

$$\mathrm{RE\ (OH_2{)}^{3+} \rightarrow RE\ (OH)^{2+} + H^+}$$

Most commercial FCC catalyst contains Y or high silica Y zeolite, mainly in rare earth and /or ammonia exchanged form. Conventional Y zeolite are synthesized with a framework SiO_2/Al_2O_3 ratio between 3 and 6 (usually about 5) while high silica Y zeolite have a higher SiO_2/Al_2O_3 ratio. Conventional Y zeolites are present primarily in gasoline FCC catalyst whereas high silica Y zeolites are used in the manufacture of octane and resid FCC catalyst.

Today, zeolites are desired catalysts because of their high concentration of active acid sites, their high thermal/hydrothermal stability, and high size selectivity. The zeolite is primarily responsible for the catalyst activity, selectivity and stability. The catalytic sites in the zeolite are strong acids (equivalent to 90% sulfuric acid) and provide most of the catalyst activity.

While cracking reactions require the presence of strong acidic sites, some secondary reaction such as isomerisation, cyclisation and intermolecular hydrogen transfer take place at weak acid sites.

The acidic sites are provided by the alumina tetrahedral. The aluminum atom at the center of each tetrahedral is at +3 oxidation state surrounded by four oxygen atoms at the corners, which are shared by the neighboring tetrahedral. Thus, the net charge of the alumina tetrahedral is -1 which is balanced by a sodium ion during the production of the catalyst. The sodium ion is later replaced by an ammonium ion, which is vaporized when the catalyst is subsequently dried and upon steaming, the unit cell undergoes framework dealumination.The equilibrium unit cell depend upon the severity of steaming and upon the type and number of cations present in zeolite.Higher steam severity result in a lower equilibrium unit cell size and low activity. The concentration, strength and distribution of acid sites in the zeolite play a key role in determining its activity and selectivity. Although the reaction that take place during catalytic cracking of gas oil are rather complex and many of the primary products undergo secondary reactions, most of these interactions involve carbocations intermediates.

3.1 Synthesis of zeolite

Today, zeolites are desired catalysts because of their high concentration of active acid sites, their high thermal/hydrothermal stability, and high size selectivity The starting materials used for the synthesis of NaY zeolite are sodium silicate, aluminum sulphate, sodium aluminate and initiator (seeds).Initiator is prepared by slowly mixing sodium aluminate solution into a solution of caustic and sodium silicate under conditions of high agitation and controlled temperature.

Zeolites are usually synthesized under hydrothermal conditions, from solutions of sodium aluminate, sodium silicate, or sodium hydroxide. Such conditions are typical of those found in the earth's crust where some zeolites are found naturally. The precise zeolite formed is determined by the reactants used and the particular synthesis conditions used, such as temperature, time, and pH; particularly critical is the templating ion, in this case the propylammonium cation. The templating ion is usually an organic cation around which the aluminosilicates lattice is formed, so that the tunnel size is determined by the templating cation. The main zeolite formula is $\mathbf{M_2/nO.Al_2O_3.xSiO_2.yH_2O}$, with M defining the compensating cation with valency n. The structural component is Mx/n [(AlO2) x (SiO2) y].zH2O, with the general structure as arrangements of tetrahedral in building units from ring structures to polyhedral.

Zeolite formation is a kinetically controlled process, and the stability goes on increasing as the energy of formation is released when the aluminosilicates with the crystallization into specific zeolite having distinct pore and exhibiting specific properties. These properties include: Ion exchange, molecular sieving, thermal/hydrothermal stability governed by silica/alumina ratio etc. Zeolites are reaction intermediates during the formation of dense phases from silica precursors. Most aluminosilicates zeolites probably could be obtained at temperatures below 100°C in alkaline solutions. This is generally the case for zeolites with a low Si/Al ratio. However, in order to reduce the reaction time (especially for zeolites with a high Si/Al ratio) and to control crystallite sizes, morphologies, and compositions, some syntheses are performed at temperatures above 100°C under autogeneous pressure in autoclaves The composition of the reaction mixture (often called reaction gel) as well as the kind of precursor materials used in the reaction mixture are very important parameters. They determine the properties of the resulting material, like for example its structure, morphology, particle sizes, particle size distribution, homogeneity of elements within the crystallites and many more. Provided the reaction time is long enough (up to some synthesis, the reaction is stopped) when the thermodynamically meta-stable zeolite has formed. Extended reaction time at high temperature and/or high pressure usually results in dense phases.

3.2 Properties of zeolite

Zeolite is sometimes called molecular sieve. It provides product selectivity and much of the catalytic activity. It has a well-defined lattice structure. Its basic building blocks are silica and alumina tetrahedral (pyramids). Each tetrahedron consists of a silicon or aluminum atom at the center of the tetrahedron, with oxygen atoms at the four corners. Zeolite lattices have a network of very small pores. The pore size of FCC Zeolite is approximately 8.0 angstroms. These small opening, with an internal surface area of roughly 600 square meters per gram, do not readily admit hydrocarbon molecules that have a molecular diameter greater than $8A^0$ to $10A^0$

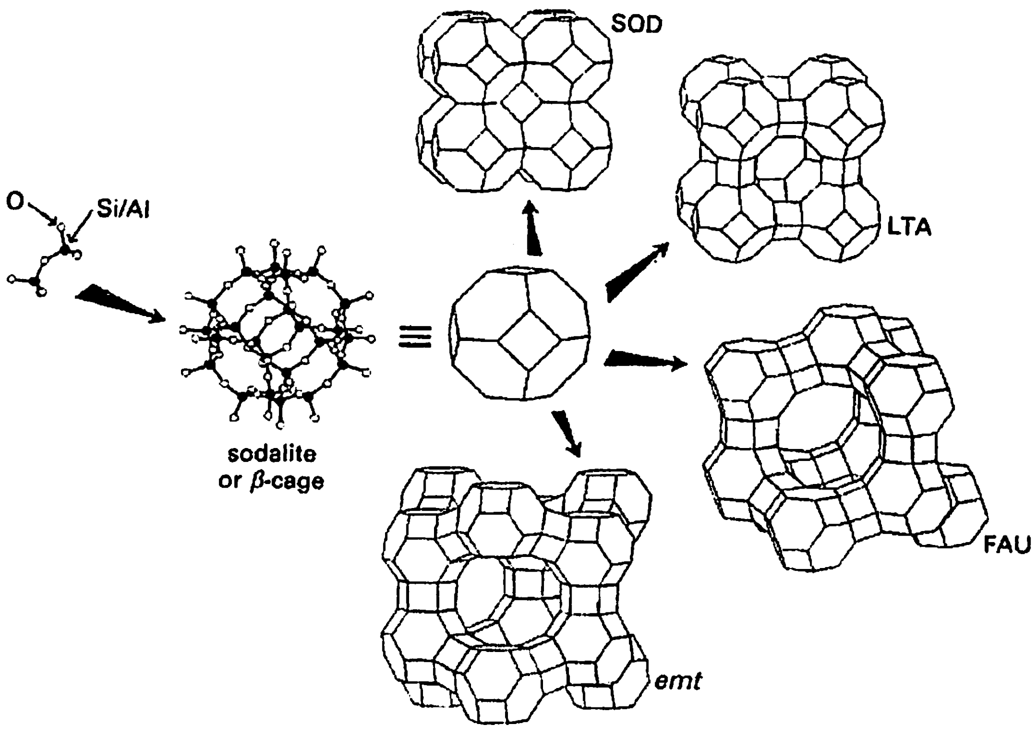


Figure 3.1 Different arrangements of Si/Al tetrahedral in catalyst geometry

Silicon is in +4 oxidation state; therefore, a tetrahedron containing silicon is neutral in charge. In contrast, aluminium is in +3 oxidation state. This indicates that each tetrahedron containing aluminium has a net charge of -1 which must be balanced by a positive ion. The sodium serves as the positive ion to balance the negative charge of aluminium tetrahedron. This zeolite is called soda Y or NaY. The NaY zeolite is not hydro thermally stable because of the high sodium content. The ammonium ion is frequently used to replace sodium.

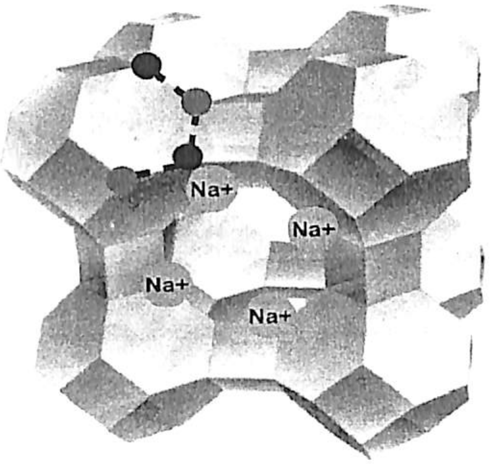


Figure 3.2 Arrangement of ions in the tetrahedral geometry

Removing most of the sodium from the zeolite is necessary in FCC catalysts because the sodium poisons active sites and makes the zeolite much less hydro thermally stable. Most of the sodium is removed by ammonium exchange using either nitrate or sulphate salts. The zeolite is also rare earth exchanged, generally with a rare earth chloride solution. Rare earth stabilizes the zeolite, with respect to dealumination, when the zeolite is exposed to heat or steam. The hydrothermal dealumination of zeolite Y was carried out to form USY (ultra stable Y).It was discovered that the hydrothermal stability of zeolite Y was highly dependent on zeolite silica-alumina ratio. The technique used wet zeolite and deep bed calcinations so that the material was self-steamed. The presence of steam promoted hydrolytic attack on the framework alumina resulting in zeolite dealumination.

3.3 Zeolite type and composition

Table 3.1 Classification of zeolites

Type of pore	**Pore size**	**Examples**
Small pore	8 ring (3.8-5.2 A)	Erionite,chabazite,phillipsite,heulandite
Medium pore	10 ring (5.4-5.6 A)	ZSM-5,ZSM-11.ferrierite,theta-1,ZSM-48
Large pore	12 ring (~7.4 A)	X,Y,mordenite,beta,offretite
Mesoporous,	16 member and above (over 10 A)	VPI, MCM

3.4 Characteristics of FCC catalysts

Modern FCC catalysts are fine powders with a bulk density of 0.80 to 0.96 g/cc and having a particle size distribution ranging from 10 to 150 μm and an average particle size of 60 to 100-μm.The designs and operation of an FCC unit is largely dependent upon the chemical and physical properties of the catalyst. The desirable properties of an FCC catalyst are:

1. Good stability to high temperature and to steam
2. High activity
3. Large pore sizes
4. Good resistance to attrition
5. Low coke production

RE, HY zeolites with over 10 wt% RE2O3 are used primarily in gasoline FCC catalyst. Raw earth content, provide high activity as compared to HSY zeolites.Because HSY zeolites have a lower concentration of acid sites than conventional ,rare earth exchanged Y zeolites.The lower acidity makes them catalytically less active. The activity of HSY zeolite can be increased by exchanging small amount of rare earth into the zeolite.

Generally REUSY (Rare earth ultra-stable Y zeolite) catalyst is used. However ZSM-5 additive contain pentasil zeolite, along with REUSY used to increase the production of LPG and C3-C4 olefins. The additive concentration in the system is typically 0.5-3 wt %. Some occasion 10-20 wt % additive is also used.

More than half of the FCC catalysts manufactured in the USA contain high silica Y (HSY)zeolites.Such zeolite are obtained by partial dealumination of conventional Y zeolites.Good quality HSY zeolite are prepared from well crystallized NaY zeolite having a SiO_2/Al_2O_3 ratio of 5 or higher. HSY zeolites used in FCC are made commercially by one of the following methods:

a) Calcinations under steam of partially ammonium exchanged Y(NH4,NaY) zeolite, leading to the formation of ultra stable Y zeolite.

b) Acid leaching of USY zeolite to obtain an ultra stable zeolite free of non-framework aluminum, and

c) Treatment of NH_4NaY zeolite with a solution of (NH_4) SiF6 (AFS) leading to the substitution of some framework aluminum with silicon from the reagent (AFSY zeolite).

Although less than conventional Y zeolites, HSY zeolites retain a higher percentage of the initial activity under severe hydrothermal treatment due to better hydrothermal stability.

Main reactions on Zeolite:

- Paraffins (cracking) to paraffin, olefins
- Olefins to LPG, Naphthenes, branched olefins, paraffin's coke

- Naphthenes to olefins,cyclo-olefins,Naphthnes of higher ring, aromatics
- Aromatics (side chain cracking, trans alkylation, condensation, polymerization) to unsubstituted aromatics olefins, poly aromatics, coke.

General Characteristics of HSY zeolites (vs. parent zeolite):

1. Increased SiO_2/Al_2O_3 ratio in framework.
2. Decrease in Unit cell size.
3. Decrease in ion exchange capacity.
4. Increase in thermal hydrothermal stability.
5. Predominant Si (OAl) group.
6. Composition gradient.
7. Increase in 2(-) value of XRD peaks.
8. Increase in frequency of IR lattice vibration.
9. Decrease in intensity of acid OH-bonds in IR spectrum.
10. Decrease in total acidity.
11. Increase in strong acidity.
12. Decrease in catalytic site density.

Typically, the FCC catalyst manufactures the following steps:

A) Zeolite preparation

B) Zeolite modification

c) Preparation of matrix

d) Mixing of all the ingredients with the binder

e) Spray drying

f) Washing the catalyst particle and exchanging with sodium

The selection of best suited catalyst is normally done in simulated micro reactor unit (simulated MAT).However the performance evaluation of FCC catalyst in simulated MAT, proper simulation of their deactivation as occurs in the commercial unit (i.e. pretreatment) is required. Therefore, development of appropriate method for hydrothermal deactivation is also equally important as that of standardization of simulated MAT activity test for its plant performance prediction.

Other properties such as presence or absence of non framework aluminium pore system, stability or composition gradient are strongly affected by the preparation method used.

The zeolite used in FCC catalysts is comprised of silica and alumina tetrahedral with each tetrahedron having either aluminum or a silicon atom at the center and four oxygen atoms at the corners. It is a molecular sieve with a distinctive lattice structure that allows only a certain size range of hydrocarbon molecules to enter the lattice. In general, the zeolite does not allow molecules larger than 8 to 10 angstroms to enter the lattice. The properties of aluminosilicates have so far been described using a number of variously extensive cluster models. The smallest possible model cluster exhibiting some characteristics common with aluminosilicates is the silicic acid molecules $Si(OH)_4$ which can be regarded as the simplest model of the basic structural unit aluminosilicates or silicates i.e. a tetrahedron.

3.4.1 FCC CATALYST COMPONENTS

There is general agreement that the higher molecular weight components are cracked either thermally or on the surface of the catalyst matrix component. The smaller molecular size products can then pass into the Faujasite zeolite for further molecular weight reduction. It is a moot point that whether this type of shape selectivity is responsible for the high activity and desirable selectivity associated with today's zeolite cracking catalysts. Until actual molecular size catalysts with pores large enough to admit gas oil feed components are discovered and developed, the validity of speculation will not be resolved.

Furthermore, process condition in the FCC unit and feedstock will also affect catalyst performance. For any given catalyst formulation, the change of process parameters during catalytic cracking will change the resulting conversion and product yields for eg.conversion increase with reaction temperature or catalyst to oil ratio and decrease with increase in space velocity.

A modern FCC catalyst has four major components: crystalline zeolite, matrix, binder and filler. Zeolite is the primary active component and can range from about 15 to 50 weight percent of the catalyst.

3.4.1.1 Matrix

Matrix plays an important role in the FCC catalyst. The basic function of matrix is to provide the base for holding the zeolite.In addition they act as the heat sink and provide strength to the catalyst particles. Very often, the matrix also possesses catalytic activity.

The active matrix is particularly useful for cracking the heavy ends of the feed hydrocarbons. Matrix also increases the metal tolerance of the catalyst. However active matrix are known to increase the gas and coke making tendency of the catalyst. Generally different types of alumina or silica alumina gels are used.

3.4.1.2 Clay

Although catalytically inactive, clay is the major part in FCC catalyst. The clay must be finely powdered and as far as possible free from iron impurities. Clay provides heat

Sink and increases the attrition resistance of the catalyst.

3.4.1.3 Binder

The name binder implies that the function of every component t is to bind all the ingredients of the FCC catalyst in the form of microspheres.Commonly used binders are silica gel, alumina sol as chlorohydrol.A good binding ensures high attrition résistance of the catalyst and prevent the removal of zeolite particles from the matrix during use.

Chapter 4

Theoretical development

4.1 Development of the additive concept

The ability of the zeolite to function as a catalyst is determined by several properties. These are the presence of active sites (acidic, basic, cationic, etc.), the spatial arrangement and size of the channels and pores, and the presence of extraneous compounds within channels of outer parts. The fact that the compound is shape-selective is due to the fact that most active sites are present in intracrystalline pores or cavities which are of molecular dimensions. The characteristics of shape selective catalysis have been traditionally applied to restricted pore zeolite such as ZSM-5 .However they can also be extended to Y zeolite based cracking catalysts as they also exhibit reactant shape selectivity. Indeed many if not most of the hydrocarbon components in a typical catalytic cracking gas oil feedstock are too large in molecular diameter to diffuse through the pore opening of the ~7.2A Y zeolite that is considered the most active component in today's cracking catalysts. ZSM-5 is used commercially as a catalyst in fluid cat-cracking (FCC) units in oil refineries to increase the motor octane of gasoline, increase the total LPG and increase the olefin content of the fraction. This is known as the secondary "cracking" of gas oil. For ZSM-5 specifically, the channels are linked by intersections, and access to the interior of the molecule occurs by 8, 10, or 12 peripheral oxygen atoms. These properties allow ZSM-5 to act as an effective "molecular sieve," In the experimental section, the formation of ZSM-5 is formed by a careful procedure of heating and purification of the product. Periodically, X-ray analyses are taken to confirm the formation of the correct product.

One of the critical questions of a ZSM-5 catalyst was whether ZSM-5 could be incorporated into a separate additive or whether it was most effective when incorporated in the same particle as the Y-zeolite.Testing showed that there was no synergy between Y and ZSM-5 and for the refiner separate additive case was attractive. The main reason for combining ZSM-5 and Y in the same particle was to reduce the effect of dilution attributable to the additional binder used in the additive. The separate particle approach was attractive mainly because it allowed much greater flexibility in ZSM-5 addition and make up rate.

4.2 Role of additives

Initially the motivation for developing a ZSM-5 changed over the course of its development. In the early 1980's lead was eliminated from gasoline which prompted a search for a means to increase octane from non-traditional sources.

FCC additives with a cracking or non-cracking function can be incorporated into the catalyst by the manufacturer, or can be added separately by the refiner. Most refiner prefer the latter approach, since it is more economical to use the additive on as needed basis. The additives most frequently used in FCC catalysis are:

- ZSM-5 based catalysts for increasing g the LPG yield;
- Octane boosting additives;
- Sox reducing additives;
- metal passivators and traps;
- CO combustion promoters.

4.3 Development of selective ZSM-5 additive

Many refiners make use of the additional propylene and butylenes for alkyl ate feed. The resulting alkyl ate usually more than offsets the gasoline loss produced by ZSM-5.Nevertheless, a demand developed in the late 1980s for an additive that produced octane shifts similar to ZSM-5 but without the gasoline losses obtained with the conventional"ZSM-5". Exxonmobil began work on such an additive in 1986 and by 1988 had commercially demonstrated "selective" version that provided similar shifts in RON and MON as has the gasoline yield loss. While some FCC operators still use this type of additive, the current focus on propylene maximization has drove most refiners to use high active phosphorous stabilization of ZSM-5:

Several researchers have demonstrated the benefits of phosphorous on the stability and shape selectivity of ZSM-5.The benefit of adding phosphorous appear to be due to its ability to retard aluminum from leaving the zeolite framework. Phosphorous reduces the initial acidity of the zeolite but after severe steaming produces a zeolite that retain a large fraction of its acidity. MAS NMR has indicated that stabilization of cracking activity is entirely due to the improved retention of framework aluminum ZSM-5.

Phosphorus has also been used as a "marker'forn the ZSM-5 additive that allow refiner to track the amount the ZSM-5 in the catalyst FCC inventory. Beginning in 1987, ZSM-5 additive manufacturer began to add phosphorous to these formulations. The effects were dramatic in improving the effectiveness of ZSM-5 and reducing the amount of additive required to achieve the desired effect on octane and light olefin yield. The increased effect translated into reduced additive costs for refiners and ultimately led to a much wider use of ZSM-5 additive.

4.4 ZSM-5 zeolite manufacture

Prior to ZSM-5, virtually all zeolite were manufactured by low temperature, atmospheric pressure synthesis. High pressure synthesis using organic directing agents were mainly the province of interest in academia and industry laboratories.

Trials were conducted at Exxon Mobil facility and were shown that gasoline RON and MON both showed increase that paralled the ZSM-5 addition rate although gasoline yield decreased however the positive effect was increase in propylene and butylenes. It is now known that the long lived resid oil octane enhancement result from the relative stable isomerisation activity of ZSM-5 compared with the shorten lived cracking activity.ZSM-5 olefin cracking activity is responsible for gasoline yield

4.5 How ZSM-5 works

ZSM-5 is a zeolite with orthorhombic symmetry, determined by model building, and single crystal or powder x-ray data. One of its important features is the ratio of aluminum to silicon. For syntheses of pH less than 10, the amount of incorporated Al increases and the Si/Al ratio is between 5 and 20. This is due to the stabilization of the structure by interactions between positive and negative charges. Likewise, as the Si:Al ratio increases, cation density and electrostatic field strengths decrease affinity of the zeolite surface for non-polar sorbates increases, as silica-rich zeolites "prefer" hydrocarbons to water

The most simplistic picture of how ZSM-5 operates in a cracking regime is based solely on its characteristic shape selectivity for cracking aliphatic (i.e. olefins and paraffin's).The intermediate size pores of ZSM-5 restrict the access of highly branched and cyclic hydrocarbons to the interior of the zeolite-5 favor the conversion of the lowest octane C5 to C7 parffins for e.g. the relative cracking rates of normal paraffin's over ZSM-5 are:

N-n-heptanes > n-hexane > n-pentane.

However the RON values of the paraffin's follows the reverse ranking. Similarly, the paraffin with high degree of branching (e.g.2, 2- and 2, 3-dimethyl butane, 2, 3- and 2, 4-dimethyl pentane) has the lower cracking rates in ZSM-5 but the higher RON values. Because ZSM-5 works as a co-catalyst converting the primary products from cracking reactions over large pore components, the reaction chemistry is not straightforward. As ZSM-5 larger pore counterpart, the Y zeolite also competes with the conversion of primary cracked products. Olefin intermediates formed by cracking heavier hydrocarbons are among the principal molecules upon which both zeolite operate.Hydrogentransfer catalyzed by the large pore zeolite frequently dictate the olefin/paraffin ratio of the cracked intermediates and therefore their reactivity. Furthermore, ZSM-5 is much less susceptible to deactivation via coking than the Y zeolite.Thus the relative activities of the two zeolite will change as the catalyst transit the catalyst zone of the unit. It is reported that the mechanism ZSM-5 deactivation is quite different from FCC catalyst. This is simply because the de-alumination of the ZSM-5 additive zeolite results in loss of active alumina but zeolite structure does not collapse with de-alumination.

The fresh FCCU catalyst always undergoes some level of hydrothermal deactivation and reaches an equilibrium state during the burning of coke in the regenerator. It is well established that FCC catalyst gets deactivated due to lattice zeolite de-alumintion and decomposition along with matrix surface collapse in the hydrothermal environment in the regenerator.

Dealumination

During preparation of HSY zeolite by steam stabilization of ammonium exchanged Y zeolite as well as during catalytic cracking process, framework dealumination takes place. The resulting non framework aluminum species and amorphous silica-alumina affect catalytic activity and selectivity.

Although the catalytic role of non framework aluminum during gas oil cracking is still debatable, it is generally agreed that its effect is both positive (higher activity, higher bottom conversion) and negative (higher coke and gas make).

Some claim that the presence of non framework alumina in steamed Y zeolites, reduction in gasoline selectivity while other claim an improvement in gasoline selectivity.

Upon steaming, the unit cell undergoes framework dealumination.The equilibrium unit cell depend upon the severity of steaming and upon the type and number of cations present in zeolite.Higher steam severity result in a lower equilibrium unit cell size and low activity.

It is found that decrease in unit cell size with corresponding dealumination corresponds to increase in framework SiO_2/Al_2O_3 ratios which favor the formation of compounds with high RON and MON octane in the gasoline fraction. It also enhances gas make and LPG olefinicity while reducing the coke make. That is why steaming is done and consequently the surface area of additive is far less than the corresponding additivecalcined, resulting in the formation of Lewis and Bronsted acidic sites.

In case of FCC catalyst, the severity of hydrothermal deactivation is applied in such a way that physico-chemical properties of laboratory deactivated catalyst should match with that of equilibrium catalyst in term of the unit cell size (UCS),%crystallinity,surface area and ASTM MAT activity.

ZSM-5 is a zeolite with orthorhombic symmetry, determined by model building, and single crystal or powder x-ray data. One of the important features of ZSM-5 is the ratio of aluminum to silicon. For syntheses of pH less than 10, the amount of incorporated Al increases and the Si/Al ratio is between 5 and 20. This is due to the stabilization of the structure by interactions between positive and negative charges. Likewise, as the Si:Al ratio increases, cation density and electrostatic field strengths decrease affinity of the zeolite surface for non-polar sorbates increases, as silica-rich zeolites "prefer" hydrocarbons to water.

Correlation between framework SiO_2/Al_2O_3 ratio and unit cell size:

The catalytic performance of the zeolite is strongly affected by its framework SIo2/AL2O3 ratio, since the ratio decreases to a large extent the concentration, strength and distribution of acid sites in the zeolite.

Due to correlation between framework SiO2/A12O3 ratio and zeolite unit cell size and the easy measurement of Unit cell size, the lattice parameters is often used to predict the catalyst activity and selectivity of the zeolite.

Most laboratory hydro thermally deactivate ZSM-5 additive at a temperature in the range of 750 to 815 degrees for 3 to 6 hours.However,few laboratories use same condition for FCC and ZSM-5 additive.

4.6 Recent ZSM-5 additive development

Additive with high level of ZSM-5 have only become commercially available in the last few years. The new ZSM-5 additive produced high level of light olefin with minimal dilution of the base cracking catalyst. Indeed Exxon Mobil conducted its own trial of a high ZSM-5 additive at its Zoliat Refinery. The results of that trial verified the values high level of highly active ZSM-5 in the inventory for the production of propylene and butylenes. More recently new generation of ultra high activityZSM-5 additives, Davison Olefin ultra has been reported to deliver high yields of propylene which allow refiner to reduce fresh catalyst addition. If coupled with improved hardware modifications such as closed cyclones improving atomizing nozzles and second row lift zones from recracking FCC naphtha, the impact of such newZSM-5 additive on propylene and butylenes makes can be magnified even further.

Chapter 5

Material and methods

5.1Experimental Details

One ZSM-5 additive slurry was prepared in the laboratory using supplementary binder based on alumina, silica, phosphate and ZSM-5 zeolite. The key ingredients and their characterized properties were as follows:

Table 5.1 Ingredients of FCCU lab additive preparation

Ingredients	Properties	
REUSY zeolite	SiO2/Al2O3 ratio	8.8
	Na2O,wt%	1.2
	Crystallinity ,%	91.4
	UCS,A	24.53
	Surface area,m2/gm	652
	RE2O3	3.8
	Crystallite size, microns	1-1.25
	LOI, wt%	7.8
Formic acid	Mol.Wt.	46.02
	Assay,%	84.5-85.5
	Density, GM/cc	1.19
	Non-volatile matter,wt%	0.04
	Chlorine.wt%	0.02
	Heavy metals and Iron,wt %	0.003

Clay	Appearance	white powder
	Sp.gravity	2.57
	LOI,wt%	15
	SiO2,WT%	45.2
	Al2O3,wt%	37.6
	Na2O,wt%	0.3
	Fe2O3,wt%	0.5
	TiO2.wt%	0.5
	Others,wt%	Balance
	Below 2 micron,wt%	87
	Below 3 micron,wt%	94
	Below 5 micron,wt%	98
	Below 7 micron,wt %	100
Alumina, Pural SB grade	Al2O3,wt%	76.89
	Surface Area,m2/gm	230
	Pore volume,cc/gm	0.05
	Average pore diameter, A	32
	LOI, wt%	23.11

5.2 Preparation of slurry

The process for the preparation of FCC catalyst comprising in the steps of preparing an aqueous alumina binder by peptising pseudoboehmite alumina with formic acid and mixing with ammonium polysilicate, aluminum depleted and normal kaolin clays and silicon stabilized rare earth exchanged zeolite to obtain a slurry, subjecting said slurry to a step of thorough mixing and spray drying to obtain microspheroidal particles, and then subjecting the particles to a step of calcination.

The zeolite component present in the additive composite is in the range of 5-35 wt %, a preferred range being from 15-30 wt %. The aluminum depleted kaolin clay is present in the range of 5-50 wt % preferred range being 15-45 wt %. The binder comprises alumina and present in the range of 10-40 wt %, a preferred range being 20-30 wt %. Kaolin clay is present in the range of 0-60 wt %, the preferred range being 0-45 wt %. The residual soda level in the finished additive is in the range of 0.2-0.7 wt %, preferred range being 0.3-0.5 wt %. The rare earth oxide content in the additive is in the range of 0.5-2 wt %, the preferred range being 0.8-1.2 wt %. The rare earth metal salts employed can either be the salt of a single rare earth metal or mixture of rare earth metals, such as chlorides consisting essentially of lanthanum, cerium, neodymium with minor amounts of samarium, gadolinium and yttrium

The final slurry was mixed homogeneously and tested for pH and solid content. This homogenized slurry was spray dried in a conventional spray drier with the following conditions:

Spray drier conditions:

Inlet temperature:	350 °C
Outlet temperature:	130 °C
Feed rate:	100 gm/min
Air supply pressure:	2 kg/cm2

Spray dried products were calcined at 500 ^{0}C before subjecting to physical characterization. Calcination program is shown in figure below. A heat rate of 4 °C/min was used during calcination.

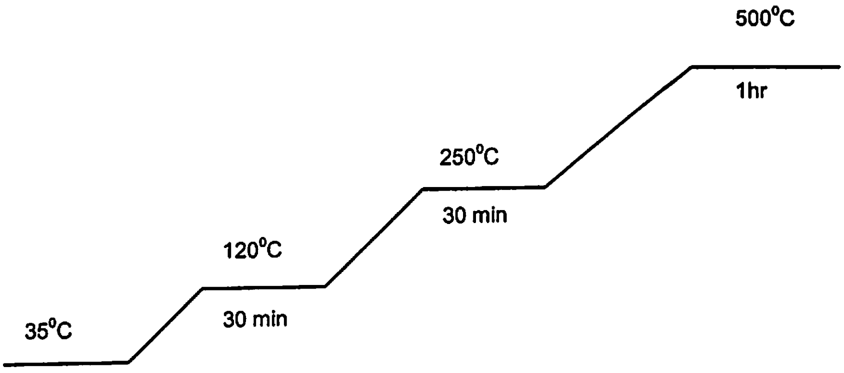


Figure 5.1: Calcination temperature profile

5.3 Analysis of physio-chemical properties

The laboratory deactivated catalyst samples were analyzed for their surface area, unit cell size and percentage crystallinity.

Alumina, Na, V, Ni, Fe present in the catalyst was measured by inductively coupled argon plasma emission spectrometer (ICAP-AES: refer Annexure 6). Surface area, pore volume, apparent bulk density, particle size distribution, percentage crystallinity and unit cell size were measured for catalyst samples by standard equipments.

The surface area is measured by determining the quantity of adsorbed nitrogen, assuming that gas forms a mono molecular layer on the catalyst surface.

For pore volume measurement, the mercury is used as the filling medium at a maximum pressure of 30,000 psia. The sample is evacuated and the mercury pressure on the sample is isostatistically increased causing the mercury to intrude into the pores. From fall of mercury level in the capillary, incremental pore volumes at different pore diameters can be obtained. Bulk density measurement is carried by filling a known volume of a cylinder with a catalyst. By taking the weight of the catalyst filled, the apparent bulk density of sample is calculated. Physical properties such as Apparent Bulk Density (ABD), Attrition Index (AI), and Surface Area (SA) of prepared were characterized and compared with commercially available additive in the

Table 5.2 Analysis of physico chemical properties

Property	**Lab ZSM-5 additive**	
Surface area,m^2/gm	Fresh	78.25
	Steamed	85.52
XRD Crystallinity,%	Fresh	11.8
	Steamed	11.0
Attrition Index(AI)		3.8
ABD,gm/cc		0.76
APS,μ(micron)		94

5.4 Performance Evaluations

Calcined additive samples were metal deactivated by using Mitchell method as given in the annexure 5 followed by steaming at 750 ^{0}C for 1 hr for a particular refinery condition (RFCC unit). Performance studies of the metal-doped steam deactivated additives were evaluated at ‘refinery RFCC’ condition in simulated MAT using 5-wt% additive with 95% wt% RFCC catalyst. Catalyst and additive blends were evaluated at different cat/oil ratio of 5.38, 6.92, and 8.46 and reaction temperature of 500 ^{0}C. From yield distributions obtained from ACE MAT (Micro Activity Test) unit, performance of additives at commercial scale was predicted with proper scale up using in-house developed FCCMOD simulator. Feed properties of RFCC unit is tabulated and given in the following table:.

The sample description used in this study is given below:

Catalyst A: Fresh Base catalyst of RFCC Refinery metal doped, H2 Reduced and steamed at 788 deg.C/ 3hrs

Additive: Fresh base additive and actual additive were metal doped, H2 Reduced and steamed at 788 deg.C/ 3hrs

Table 5.3 Analysis of a Refinery Y feed

Feed properties of RFCC unit	
Density at 15 ^{0}C (gm/ml)	0.855
Distillation,	
%Vol	^{0}C
IBP	337
10	394
50	473
90	548
FBP	562
Aromatics, wt%	34.5
Olefins, wt%	0
Saturates, wt%	65.5
Sulfur, wt%	0.15
CCR (wt%)	< 0.1
Vanadium, ppm	< 1
Nickel, ppm	Nil

5.5 RFCC method

A series of experiments were conducted whereby base catalysts i.e. the equilibrium catalysts from Refinery Y was tested for their physio-chemical properties and then evaluated in the ACEMAT.

The micro activity test (MAT) unit was originally designed to determine the activity and selectivity of either equilibrium or laboratory deactivated fluid catalytic cracking (FCC) catalysts. Currently, the MAT unit is accepted as a tool to perform general laboratory scale FCC research and testing because of its simple operation and cost effectiveness. The unit only requires small quantities of catalyst/additive and gas oil for each MAT test, compared with barrels of materials needed for a pilot-scale riser run.

The deactivation rates are higher for catalyst in units with higher temperature, higher steam partial pressures, higher average age of circulating inventories and higher contaminant metals like sodium, nickel, vanadium etc. (Ref 1). All of the above have significant effect on the performance and the stability of the catalyst and hence FCC unit performance.

One of the challenges in evaluating new FCC catalyst technologies has been in simulating how the catalyst will perform after being deactivated in a commercial FCC unit. The average catalyst age in the inventory of a commercial unit that replaces 2% of the inventory everyday is 50 days. Lab methods are designed to accelerate this aging process and accomplish the results in few hours. The general strategy to accelerate the aging is to increase the temperature and steam pressure during aging. The "deactivation" in commercial unit is caused by hydrothermal environment (typically 700-deg c, 20 % steam) in the "regenerator".

5.5.1 FCC Catalyst Deactivation Mechanisms

There are two types of catalyst deactivation, which occur in FCC systems - reversible and irreversible. Reversible deactivation occurs due to coke deposition each time the catalyst passes through the reactor, and is reversed by coke burning in the unit's regenerator. What is addressed here is the longer term, irreversible deactivation of the catalyst as it ages in the unit. This can be viewed as a combination of four separate, but interrelated, mechanisms:

1. Zeolite dealumination

2. Zeolite decomposition

3. Matrix surface collapse

4. Contaminant effects

Zeolite dealumination, as measured by unit cell size reduction, reduces the acid site density and hence, the inherent activity per unit of zeolite. Zeolite decomposition, measured by crystallinity or micro pore surface area loss, also reduces activity. Both processes occur simultaneously in the hydrothermal atmosphere of an FCC regenerator. As will be discussed later, they are not independent. Matrix surface area collapse reduces activity by reducing catalytically active matrix sites, as well as by reducing porosity of the particle, which can restrict accessibility of the zeolite. Contaminants such as vanadium and sodium also contribute to deactivation in various ways.

Catalyst deactivation in the presence of metals is usually done by impregnating the catalyst with vanadium and nickel, which are predominant contaminants in commercial RFCC operation. Vanadium is the more critical of the two metals in lab deactivation because it has two effects: vanadium destroys the zeolite and catalyses dehydrogenation reactions. The magnitude of both effects depends on the oxidation state of vanadium. In the +5 state, vanadium reacts to form vanadic acid (H_3VO_4) under the hydrothermal conditions in FCC units. Vanadic acid has intra-particle and inter-particle mobility and penetrates and destroys the zeolite much more effectively than vanadium at lower oxidation states. Moreover, the formation of hydrogen and coke is exaggerated by vanadium in the +5 state compared with the dehydrogenation activity of nickel. In commercial operation, vanadium can be in either +4 or +5 state. The ratio of the time the vanadium is in these two oxidation state depends on regenerator condition and this complicates lab deactivation. Nickel is less critical because it does not attack the zeolite. It has only a dehydrogenation activity, which is less effected by oxidation state.

The first approach for metallation and ageing of FCC catalyst discovered was the Mitchell technique. In this experiment, vanadium is in the +5 state, continuously, and therefore, this method exaggerates the effects described above. In order to improve the simulation of commercial deactivation in the lab testing, circulating pilot units were designed in which the FCC catalyst were metallated by cracking of vacuum gas-oils spiked with contaminant metals. The metallated catalysts were aged with reduction-oxidation cycles. It was shown that the performance of catalyst deactivation in such units represents commercially equilibrated catalyst much more realistically than Mitchell technique. However, cyclic metallation and ageing in pilot units is time consuming and the complexity of such unit's impairs the reproducibility of experiments. Hence the use of this technique is usually discouraged. In this experiment Mitchell method was used to carry out the deactivation and metal impregnation to the sample.

5.5.2 Laboratory Deactivation

Laboratory deactivation of fresh FCC catalyst is accomplished by steam treatment at elevated temperatures to accelerate the hydrothermal aging, which occurs in a commercial regenerator. Steaming conditions are typically chosen to achieve a steamed property such as MAT activity, zeolite unit cell size, or surface area, which targets typical equilibrium catalyst properties. A wide range of streaming conditions is used in the industry. However in order to reduce the time from the commercial conditions different laboratories have been using different type of deactivation procedure based on their requirements.

Engelhard laboratory studies have shown that relative laboratory performance rankings of catalyst are most influenced by the severity of the streaming treatment (Ref.1). In particular, coke selectivity rankings show a large dependence on the streamed catalyst properties tested. Therefore, it is a very important to properly reflect anticipated equilibrium properties in the catalysts tested. One area, which is commonly neglected in laboratory testing, is the effect of catalyst age distribution. Because the nature of FCC unit operation dictates that a fraction of the catalyst inventory be replaced with fresh catalyst on a continual basis, a distribution of properties reflecting the age distribution will exist in any equilibrium sample. Measured bulk properties are , therefore, averages. Laboratory steamed samples, which appear to match these bulk average properties, may still perform differently if they do not match the property distribution.

Following methods were used in the current study for the laboratory deactivated sample data.

5.5.2.1 Mitchell Method:

Steps:

1. The physical properties of the catalysts are analyzed.
2. The sample is calcined at 590 deg C for three hours to remove moisture and any adsorbed chemicals
3. Doping of metal
    a. Based on liquid analysis of octuate, the amount required is calculated
    b. The catalyst sample is weighed and taken in a beaker
    c. A required amount of both the octuates, as calculated above, is taken in a beaker.
    d. Required amount of toluene is taken and added to the octuates (calculate using pore volume)
    e. The above mixture is poured in the catalyst sample while stirring.
    f. The beaker containing the octuates is rinsed with toluene and contents poured into the catalyst sample while stirring continuously.
    g. The sample was dried on a heater plate while continuous stirring so as to ensure that heating is uniform throughout.
    h. The sample is calcined at 538 deg C for one hour to decompose and vaporize all the hydrocarbons added along with the metal octuates

4. The catalyst sample is then sent for analysis to determine the metal levels.

The details of the Mitchell method are given in Annexure-4.

5.5.2.2 Cyclic Deactivation Method (Refer annexure 1)

Principle: In commercial FCC unit, metals are deposited cyclically on catalyst particles in a sequential operation of reaction, stripping and regeneration. Cyclic Deactivation Unit (CDU) is also designed to operate in similar fashion and in simulated conditions as exist in commercial RFCC unit.

Steps: It consists of three steps, namely, reaction, stripping and regeneration.

Reaction: About hundred grams of the catalyst to be tested is loaded in the reactor Vessel. Desired reaction temperature (525 deg C) is set and continuous flow of nitrogen is maintained to keep the catalyst in good fluidized condition. Once the steady state is reached, the feed injection system is activated at this point and the desired quantity of metal loaded feed (pre heated to around 300 deg C) is injected in a set time. In this process, cracking of the feed takes place in presence of the catalyst. This results in deposition of coke and metals on catalyst.

Stripping: the nitrogen flow (fluidizing media) is continued for a definite time to strip off any interstitial hydrocarbon vapors. All the operating conditions are nearly the same as the reaction step.

Regeneration: Once the stripping is completed, unit is switched over to pre regeneration mode, where the regeneration temperature (~ 750 deg C), time and airflow are set as per the requirement. In addition, steam generation temperature is also set. As soon as the desired conditions are reached, regeneration is started. During regeneration, steam is also injected for maintaining the steam partial pressure, same as a commercial FCC regenerator. After regeneration is over, system is cooled to reaction temperature and the same procedure is repeated for desired number of cycles. The detail of this method is explained in Annexure-5.

As the severity of regeneration in CDU is not enough to simulate the deactivation of catalyst to equilibrium level, it is required to be steamed at 788 deg C for three hours before proceeding to a later analysis.

Hydrothermal treatment

The metal doped and reduced sample was given it for steam deactivation at 788 deg.C / 3hrs with 100% steam. The detail method is explained in Annexure-1.

5.6 MAT Evaluation

In the current study, evaluation runs were conducted in ACEMAT (refer Annexure 6) unit. The ACE Model R+ uses a sophisticated and fully automatic process to emulate commercial FCC performance (i.e. to carry out MAT). It employs a cyclic operation of a single reactor (containing a batch of fluidized catalyst particles) to simulate the conditions of FCC unit.

The catalyst / additive sample is then send for metal analysis (5 gms for XRF analysis) to determine the metal levels obtained. The acceptable range is ± 10% of the targeted level. Details related to calculation of octuates amount required.

Basis: 30 gms

Wt. of the catalyst = 30 gms.

Conc. of Ni in nickel octuate = X wt%

Conc. of V in Vanadium octuate = Y wt%

Targeted Ni = **3500 ppm**

Targeted V = **7000 ppm**

Ni octuate is to be taken, L = **(30*3500*10^{-6}*100)/ X gms.**

V octuate is to be taken, M = (30*7000*10^{-6}*100)/ Y gms.

Oil, nitrogen, air and a reducing gas are supplied during well defined steps of cracking cycle. In this way, the batch of cracking catalyst experiences the same reactions and temperature as does catalyst material circulating through out the reactors of a refinery in a FCC unit. The laboratory operation is characterized by the following steps:

- Injection of oil over catalyst.
- Catalyst stripping for a specified duration.
- Catalyst regeneration with air at elevated temperatures.
- An optional reaction of the catalyst with the reducing gas at a prescribed temperature to control the oxidation state of contaminant metal on the catalyst.

Gas and liquid products are analyzed respectively in **on-line GC and simulated distillation analyzer** (refer annexure 5). Coke deposited on the catalyst is quantified during regeneration by analyzing for the amount of CO_2 in flue gas using an on-line IR analyzer.

Table 5.4 Plant Performance Yield of lab ZSM-5 additive for RFCC unit

(Propylene maximization)			
Basis: Equal Plant Coke Level			
Parameters	**BASE**	**BaseCat + Base ZSM-5**	**BaseCat + lab ZSM-5**
R&D Reference No.	CE-11972	CE-11972 + CE-14774	CE-11972 + CD-10842
Catalyst composition, wt%	100%	85%+15%	85%+15%
Yield, wt% (FF Basis)			
Dry gas	3	3.86	3.34
LPG	20.8	30.57	29.68
Gasoline	37.5	35.52	37.47
HN	2.8	2.55	2.52
LCO	22.3	17.25	17.35
TCO	25.1	19.8	19.87
CLO	8.3	4.77	4.11
Coke	5.3	5.48	5.53
216 Conversion, wt%	69.4	77.98	78.54
	100.00	100.00	100.00

Process Conditions			
Fresh Feed Rate, M3/hr	108.2	124.8	124.8
HCO Recycle, M3/hr	9	18	18
Feed Preheat Temp., °C	258	270	270
Riser Top Temp., °C	510	511	511
Regen Temp., °C			
Dense1/Dense2	648/708	661/714	670/727
CRC, wt%	0.05	0.04	0.048
Cat. Circ rate, MT/hr	558	637	595
Cat/Oil ratio	5.92	5.89	5.50
MAB Air, NM3/hr			
RG-1	27578	35578	35578
RG-2	20777	21777	21777
Propylene yield, wt%	**5.16**	**7.15**	**7.63**
Propylene in LPG, %	24.80	23.38	25.71

6.0 RESULTS AND DISCUSSION

1. It was observed that SA, ABD and AI of prepared ZSM-5 additive are 85.52 m2/gm,94 and 3.8 which are well within the specified limits.
2. Dry gas yield of prepared ZSM- 5 additive is 0.5 wt % higher than of base ZSM-5 additive.
3. LPG selectivity of lab prepared ZSM- 5 additive is 0.89 wt % lower but gasoline selectivity is 1.95 wt % higher than that of base ZSM-5 additive.
4. Propylene in LPG of lab prepared ZSM- 5 is 0.45 wt % higher than the base ZSM-5 additive.
5. Bottoms yield for lab prepared ZSM-5 is also decreased marginally compared to base ZSM-5 additive.

7.0 CONCLUSIONS

ZSM-5 additive mainly function by selectively cracking the heavy oil components and increase the lighter olefins content affecting both gasoline octane and light olefins components particularly propylene which is of great demand and of great economical value.

More precise catalyst formulations should be tried to further optimize the yield of propylene out of the the shape selective ZSM-5 catalyst-additive formulations.

Table-5.5 Yield of different products with different catalyst and additive combinations

Run No.	*621*	*622*	*623*	631	632	633	694	696	695
Date	*02.04.2009*	*02.04.2009*	02.04.2009	06.04.2009	06.04.2009	06.04.2009	05.05.09	05.05.09	05.05.09
Catalyst I.D.	100%	100%	100%	(85%+15%)	(85%+15%)	(85%+15%)	85+15	85+15	85+15
Catalyst Name	11972MD-413AS1820	11972MD-413AS1820	11972MD-413AS1820	11972+CE-14774	11972+CE-14774	11972+CE-14774	11972+CD-10842	11972+CD-10842	11972+CD-10842
Feed I.D.	CE-18472	CE-18472	CE-18472	CE-18649	CE-18649	CE-18649	CE-18469	CE-18469	CE-18469
Feed Name	RFCCU	RFCCU	RFCCU	RFCCU	RFCCU	RFCCU	RFCCU	RFCCU	RFCCU
Cracking Temperature, °C	511.0	511.0	511.0	511.0	511.0	511.0	511.0	511.0	511.0
Injection Time, sec	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Catalyst Strip Time, sec	360	360	360	360	360	360	360	360	360
Liquid Strip Time, sec	600	600	600	600	600	600	600	600	600
Injector Position, inches	1.125"	1.125"	1.125"	1.125"	1.125"	1.125"	1.125"	1.125"	1.125"
Catalyst-to-Oil, wt/wt	4.51	6.02	7.52	4.51	6.02	7.52	4.51	6.02	7.52
YIELDS, wt%:									
Dry Gas	1.629	1.932	2.217	1.610	1.890	2.175	1.642	1.866	2.294
Hydrogen	0.292	0.328	0.376	0.252	0.293	0.344	0.247	0.350	0.356
Hydrogen Sulfide	0.228	0.228	0.228	0.228	0.228	0.228	0.228	0.228	0.228
Methane	0.320	0.401	0.483	0.294	0.356	0.437	0.252	0.343	0.394
Ethane	0.279	0.333	0.395	0.248	0.298	0.354	0.224	0.275	0.345
Ethylene	0.510	0.642	0.735	0.587	0.713	0.811	0.691	0.671	0.972
Propane	0.899	1.178	1.389	1.114	1.395	1.585	1.244	1.346	1.816
Propylene	**4.794**	**5.373**	**5.603**	**6.158**	**6.702**	**6.989**	**7.451**	**7.746**	**8.477**
n-Butane	0.993	1.267	1.445	1.137	1.350	1.496	1.133	1.295	1.528
Isobutane	4.448	5.543	6.145	5.388	6.343	6.940	5.842	6.334	7.790
C4 Olefins	6.417	6.729	6.751	7.521	7.723	7.741	8.556	9.204	8.967
1-Butene	1.304	1.365	1.369	1.474	1.499	1.507	1.552	1.700	1.615
Isobutylene	1.618	1.620	1.588	2.039	2.038	2.000	2.574	2.607	2.651
c-2-Butene	1.454	1.554	1.574	1.664	1.735	1.752	1.836	2.031	1.945
t-2-Butene	2.041	2.190	2.221	2.343	2.451	2.482	2.594	2.866	2.755
Butadiene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
LPG	17.552	20.090	21.334	21.318	23.512	24.752	24.226	25.924	28.577
Gasoline (C5-150°C)	28.881	30.628	31.770	30.416	31.530	30.897	27.877	30.487	30.624
Heavy naphtha (150-216°C)	12.175	11.433	10.869	11.978	11.679	11.816	9.035	8.735	8.144
Light cycle oil (216-370°C)	18.767	16.890	15.718	15.995	14.705	14.252	19.373	16.976	15.722
Clarified Oil (370°C+)	12.573	9.960	7.927	11.329	8.513	7.149	11.181	8.367	6.713
Coke	8.423	9.067	10.165	7.353	8.171	8.958	6.666	7.644	8.927
Conv., wt%	68.66	73.15	76.35	72.68	76.78	78.60	69.45	75.36	77.57
Recovery, wt%	101.8	102.7	103.7	102.5	104.3	103.7	102.1	101.7	102.0
TOTAL	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000

TABLE 5.6 : MAT DATA

BASE(OF)								
CONV	**5.505**	-0.2778	5.8982	47.71	**71.76**			
COKE	**5.505**	6.3126	0.0624		**8.90**			
						1.00		
DG	**71.76**	0.1051	0.0399		1.84	**1.85**		
LPG	**71.76**	3.0305	0.0257		19.16	**19.24**		
GAS	**71.76**	-0.0043	0.995	-19.295	29.96	**30.09**		
HN	**71.76**	-0.0014	0.0293	16.631	11.52	**11.57**		28.23914
LCO	**71.76**	0.0068	-1.3822	81.616	17.45	**17.49**		28.17483
CLO	**71.76**		-0.6024	53.958	10.73	**10.75**		1.002283
COKE	**71.76**	1.6146	0.0239		8.97	**9.01**		
					99.64	**100.00**		
					71.46	**71.76**		
BASE+BASE ZSM-5 (NF)								
CONV	**5.505**	-0.5013	7.9984	46.8	**75.64**			
COKE	**5.505**	5.4819	0.0656		**7.87**			
						1.01		
DG	**71.76**	0.0461	0.0488		1.53	**1.54**		
LPG	**71.76**	3.464	0.025		20.83	**21.01**		
GAS	**71.76**	-0.1047	15.913	-573.32	29.45	**29.70**		
HN	**71.76**	0.0251	-3.8215	157.24	12.26	**12.37**		28.23914
LCO	**71.76**	0.011	-1.9555	100.11	16.43	**16.32**		28.41665
CLO	**71.76**		-0.7024	62.394	11.99	**11.91**		0.993754
COKE	**71.76**	0.7124	0.032		7.08	**7.14**		
					99.56	**100.00**		
					71.15	**71.76**		
BASE+LAB ADDITIVE (ce-10814) - NF								
CONV	**5.505**	-0.4695	8.6481	40.709	**74.09**		1.032	
COKE	**5.505**	4.9455	0.0653		**7.08**		0.796	
						0.99		
DG	**71.76**	0.2261	0.0292		1.84	**1.82**	-0.03	
LPG	**71.76**	3.7152	0.0256		23.32	**23.13**	3.89	
GAS	**71.76**	-0.0067	1.2951	-28.316	30.12	**29.87**	-0.22	
HN	**71.76**	-0.0513	7.4981	-263.68	10.21	**10.13**	-1.44	28.23914
LCO	**71.76**	-0.02	2.4897	-57.099	18.57	**18.77**	1.29	27.93808
CLO	**71.76**		-0.4921	44.68	9.37	**9.47**	-1.29	1.010776
COKE	**71.76**	1.5413	0.0208		6.86	**6.80**	-2.21	
					100.29	**100.00**	**0.00**	
					72.35	**71.76**	**0.00**	
BASE+LAB ADDITIVE (ce-10842)-NF								
CONV	**5.505**	-0.8112	12.456	29.77	**73.76**		1.028	
COKE	**5.505**	4.2894	0.097		**7.32**		0.822	
						0.99		
DG	**71.76**	0.1217	0.0372		1.76	**1.74**	-0.11	
LPG	**71.76**	6.6424	0.0185		25.05	**24.76**	5.51	
GAS	**71.76**	-0.0467	7.211	-247.44	29.54	**29.19**	-0.90	
HN	**71.76**	-0.0267	3.8165	-127.2	9.18	**9.07**	-2.50	28.23914
LCO	**71.76**	-0.0509	7.0795	-226.63	19.29	**18.58**	1.10	29.30542
CLO	**71.76**		-0.5349	48.405	10.02	**9.66**	-1.10	0.963615
COKE	**71.76**	0.6503	0.0333		7.09	**7.01**	-2.00	
					101.93	**100.00**	**0.00**	
					72.63	**71.76**	**0.00**	

FIGURE-5.1
CAT/OIL vs CONVERSION

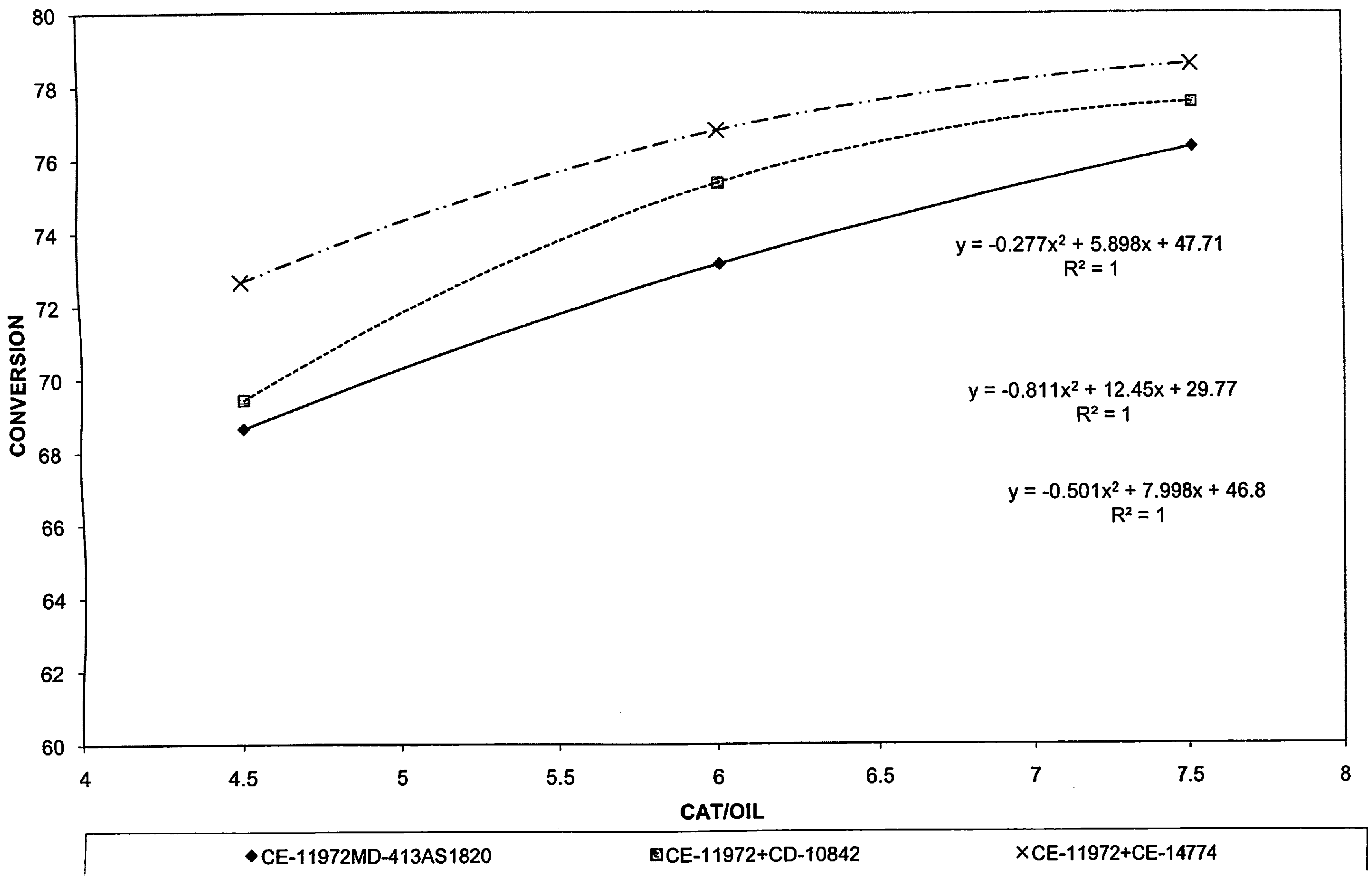


FIGURE-5.2
CAT/OIL vs COKE

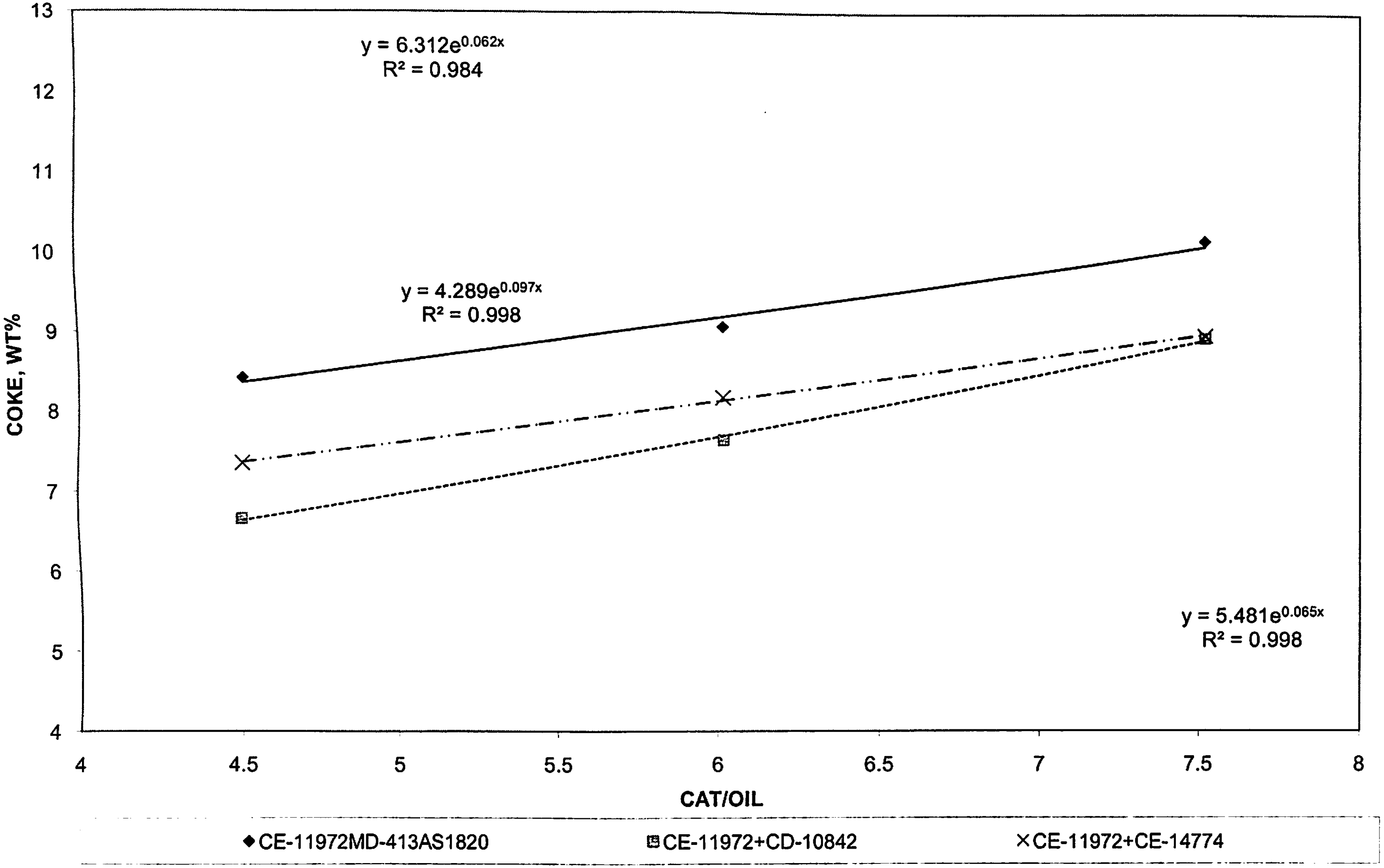


FIGURE-5.3
CONVERSION VS COKE

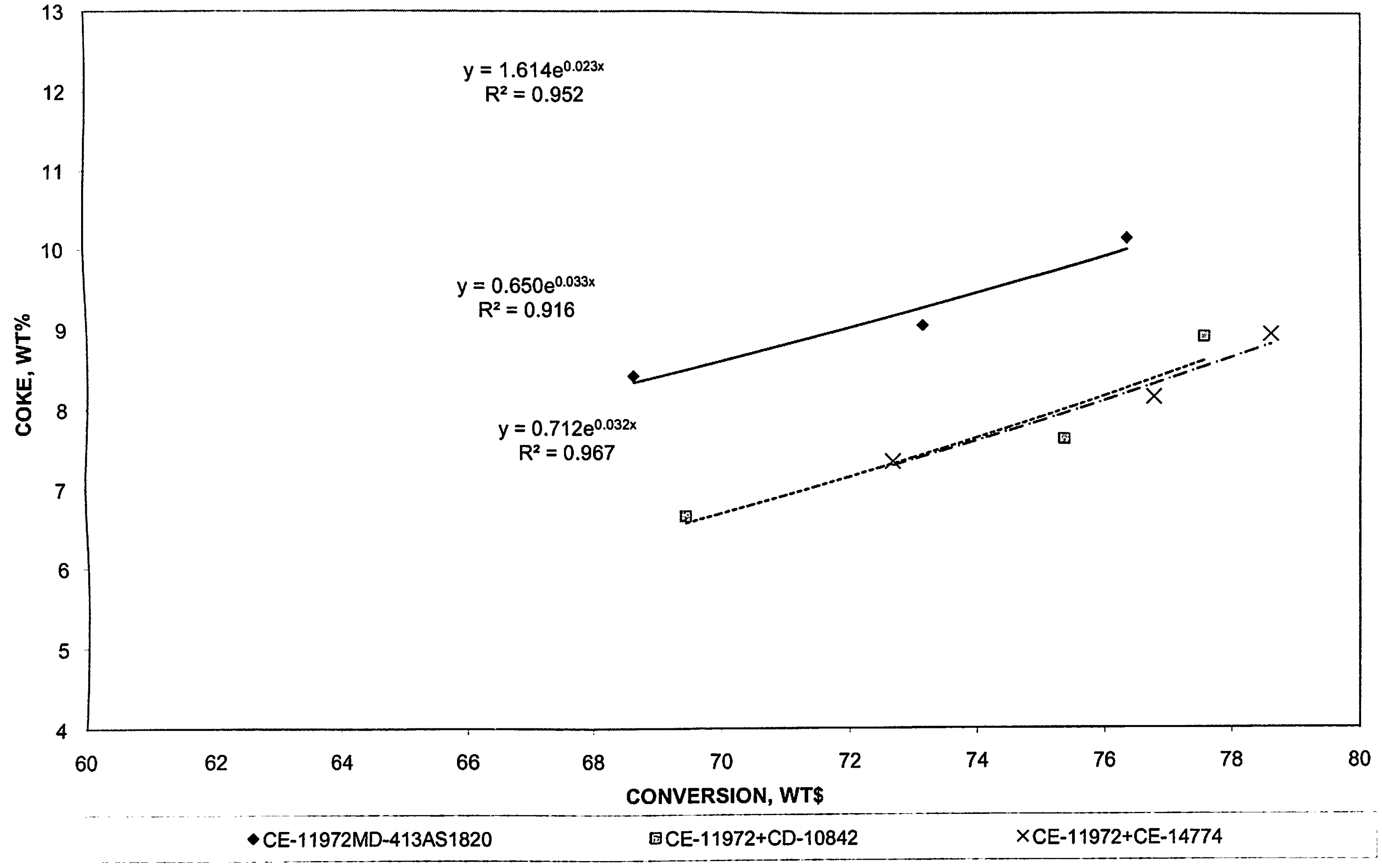


FIGURE-5.4
CONVERSION VS DG

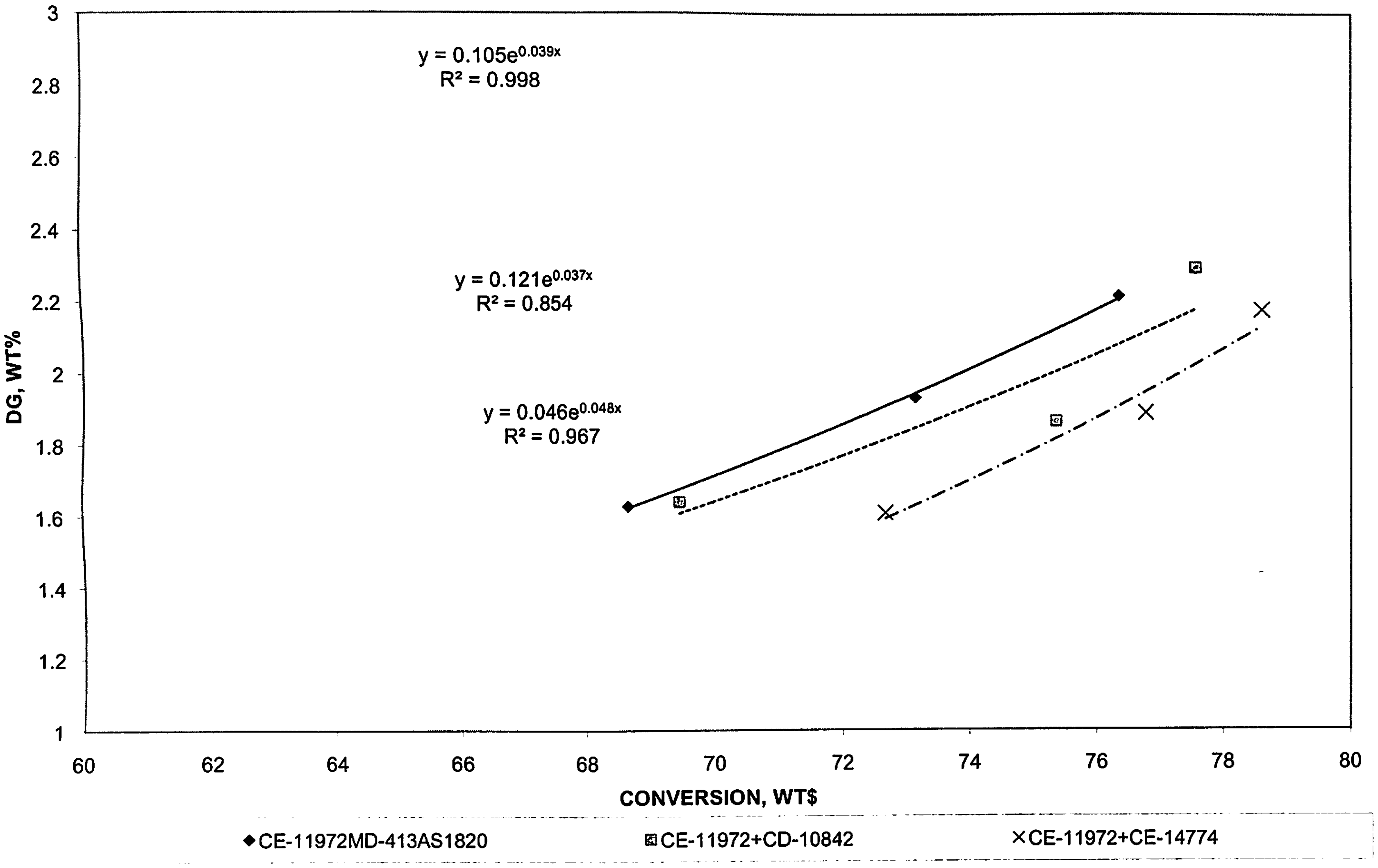


FIGURE-5.5
CONVERSION VS LPG

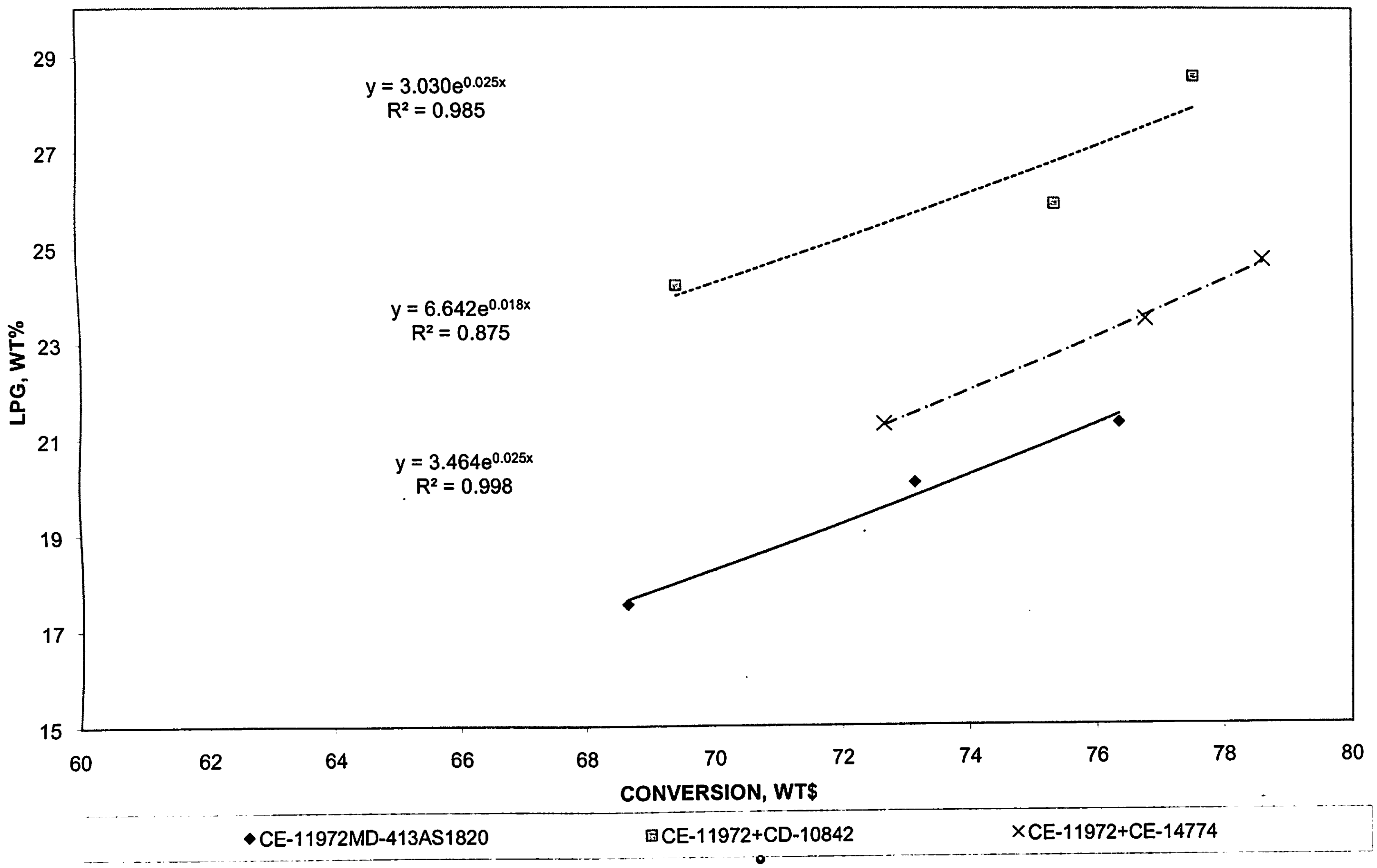


FIGURE-5.6
CONVERSION VS GASOLINE

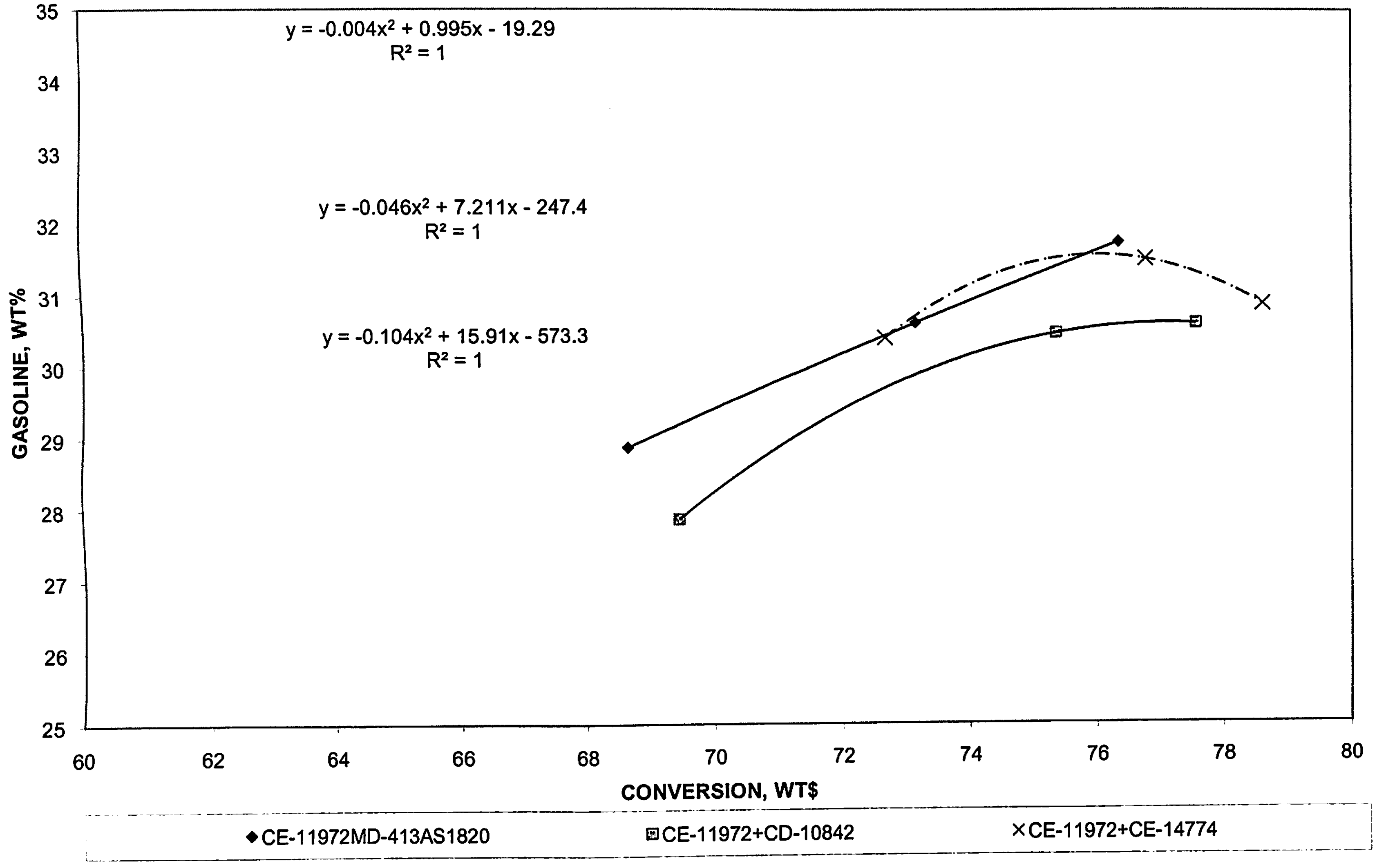


FIGURE-5.7
CONVERSION VS HN

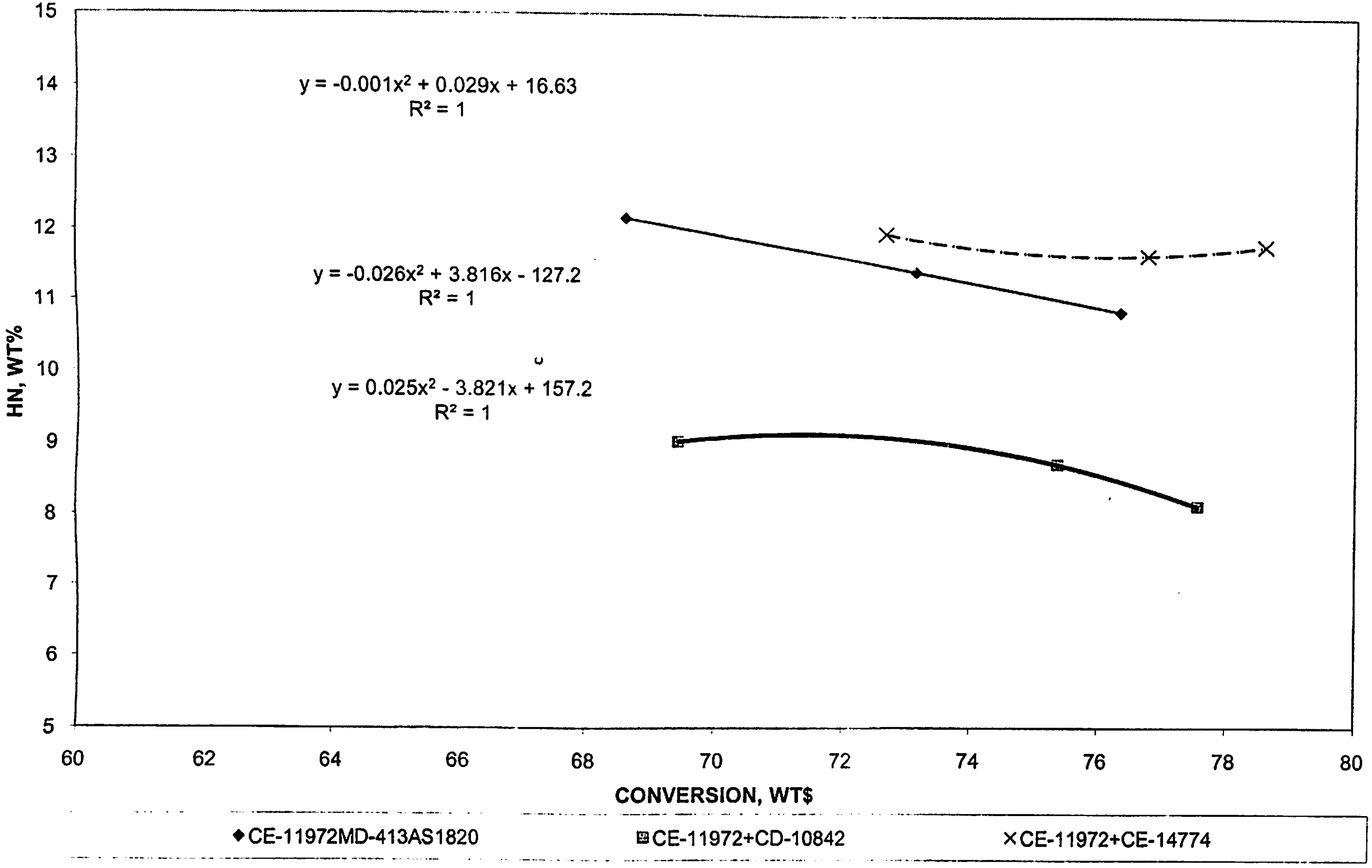


FIGURE5.8
CONVERSION VS LCO

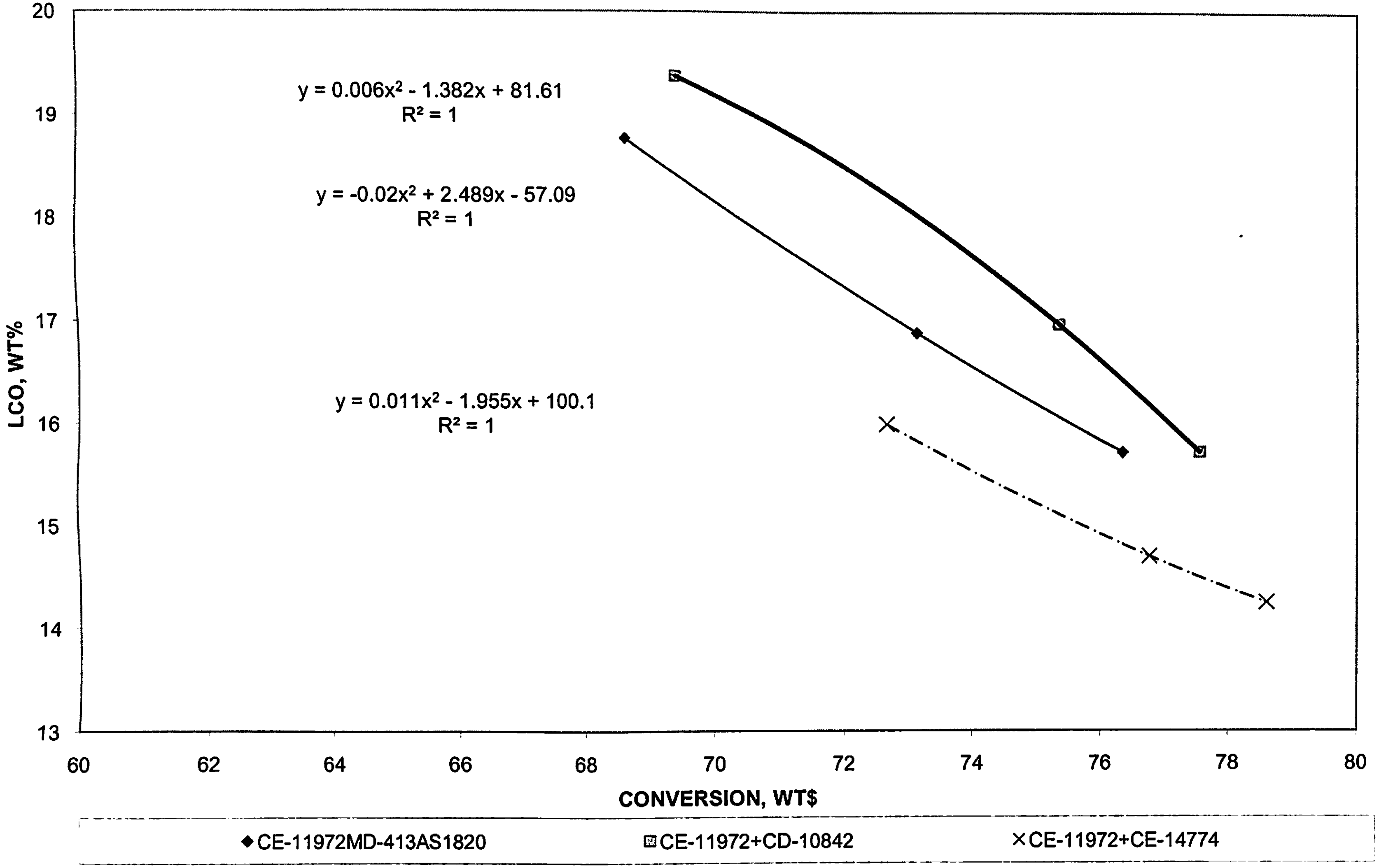


FIGURE-5.9
CONVERSION VS LCO

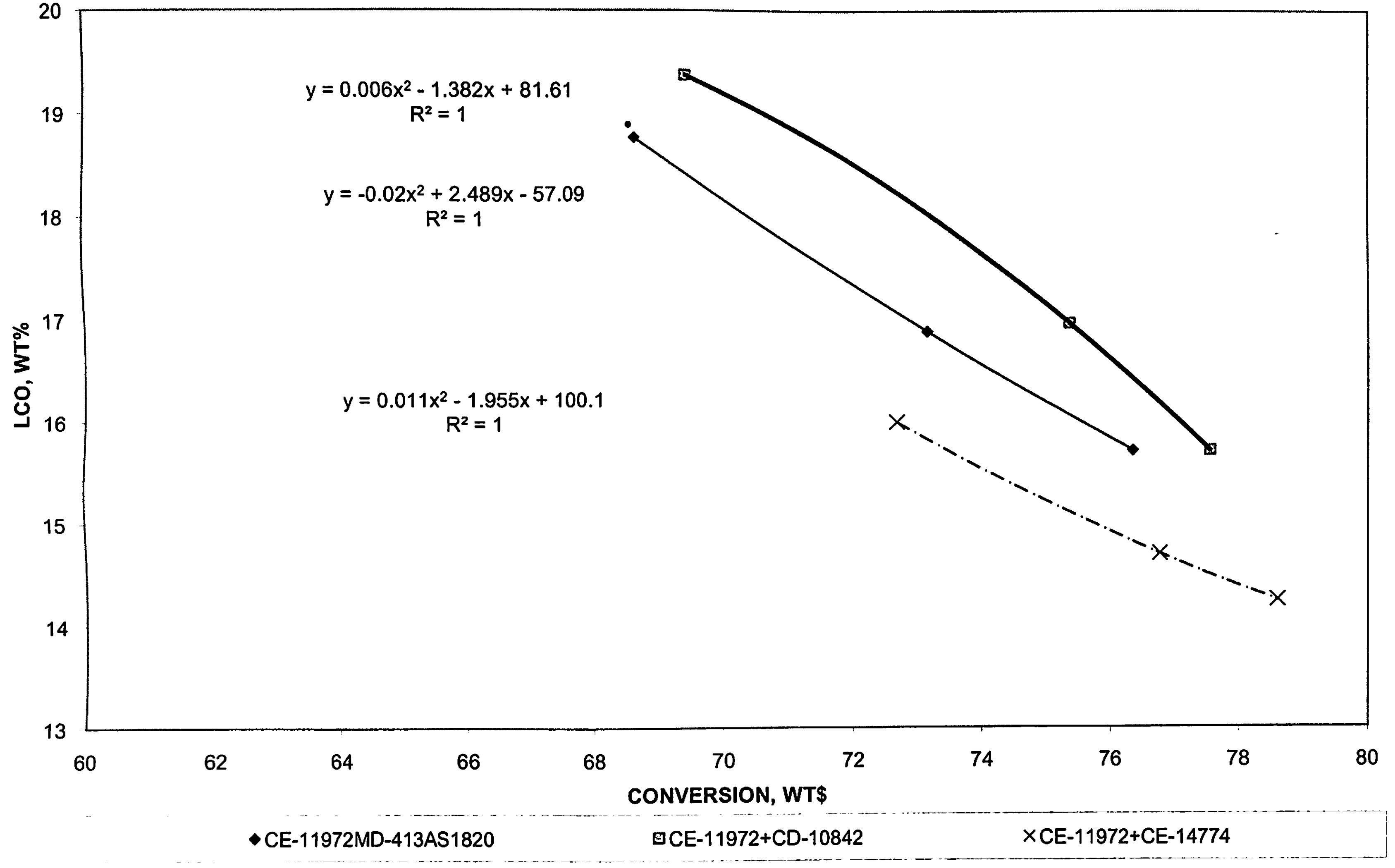


FIGURE-5.10
LPG VS PROPYLENE

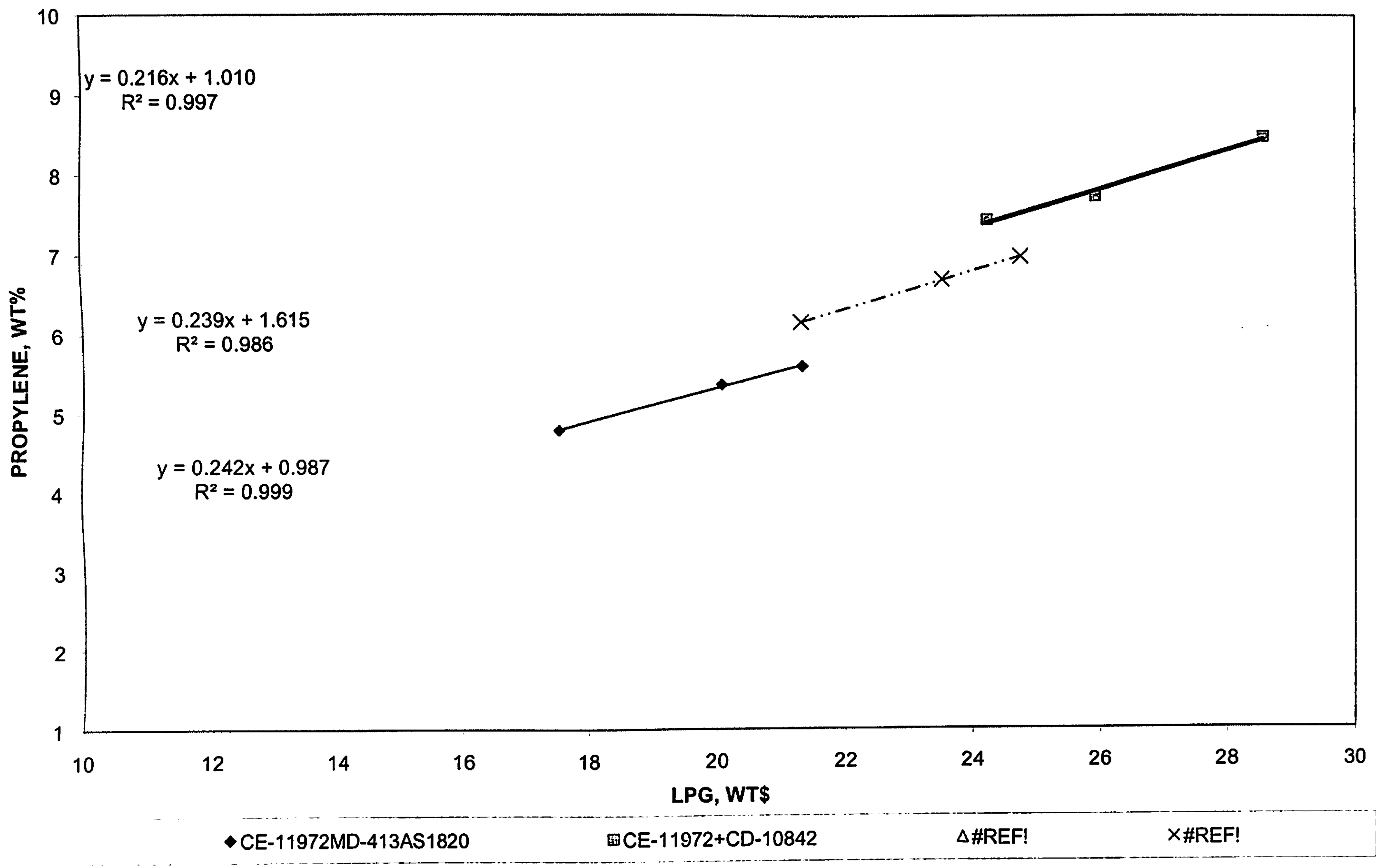


FIGURE-5.11
LPG VS PROPYLENE

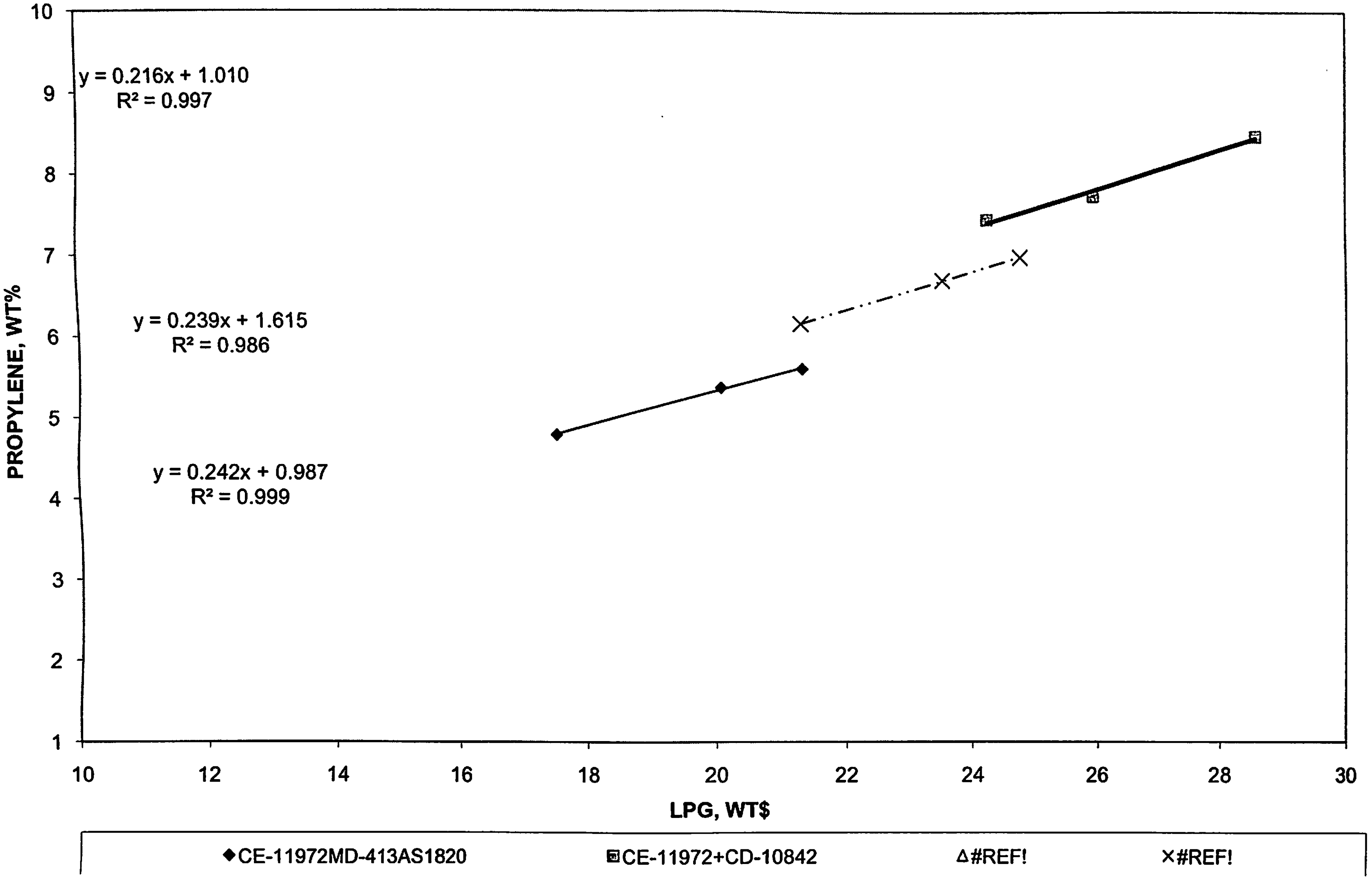
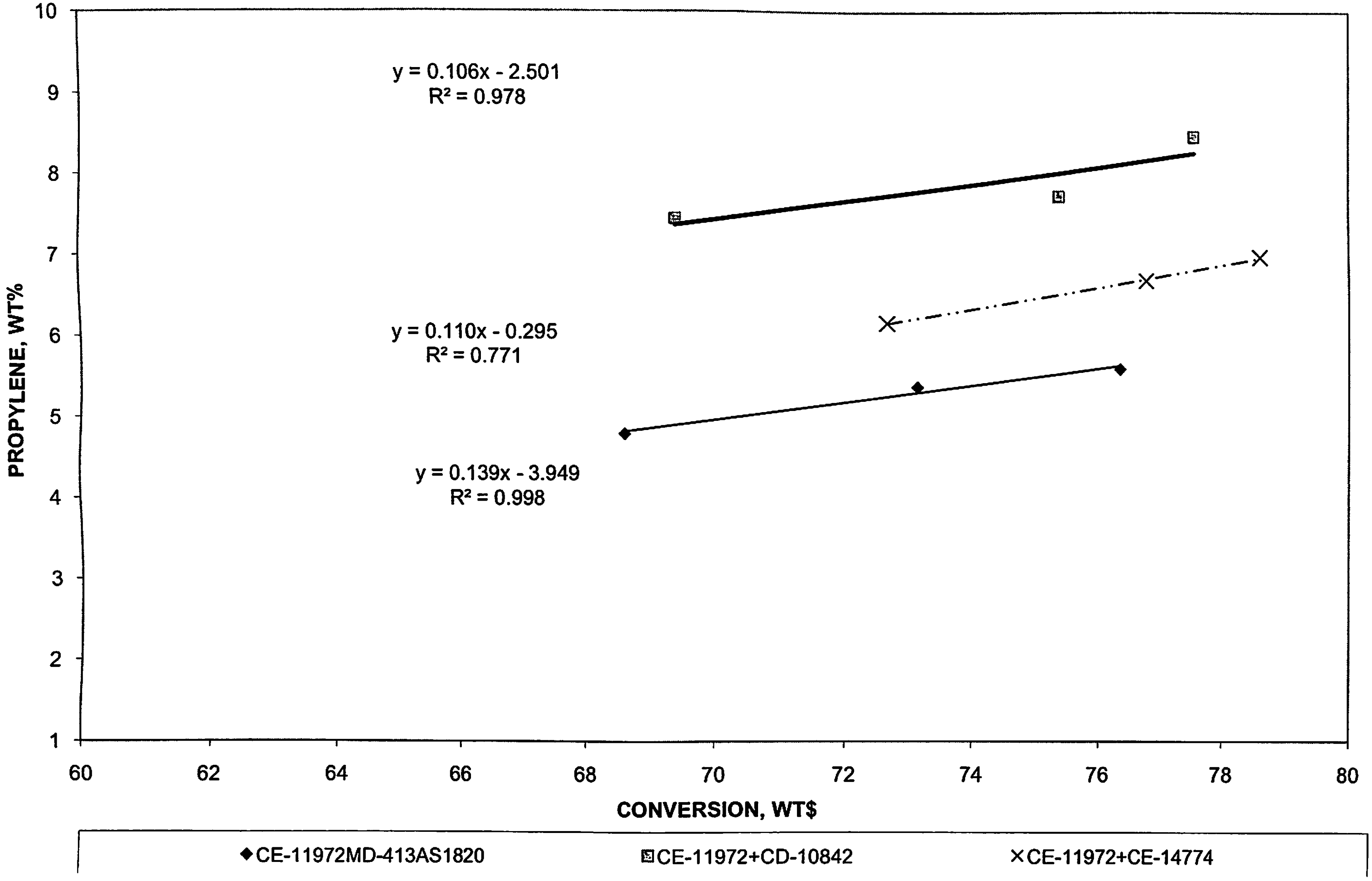


FIGURE-5.10
CONVERSION VS PROPYLENE



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ANNEXURE-1

STEAMING UNIT:

INTRODUCTION

Steam deactivation of FCC catalyst is the reduction of activity of fresh FCC catalyst by processing them for a specified period of time in the presence of steam at a defined temperature. The steaming process will decrease both the surface area and catalytic activity of the catalyst. The objective of the steam deactivation is to get a catalyst of plant equilibrium activity as obtained in the commercial units and also to check the hydrothermal stability of the fresh commercial as well as laboratory-developed catalyst and additive.

DETAILS/ PROCEDURES:

Unit is calibrated on after every 30 runs. Required quantity of solid sample (20±5 gms) is loaded in the steaming reactor. The reactors are placed in the furnace and the nitrogen/water line is connected to the reactor. The furnace top is covered with ceramic blanket insulation to reduce the heat loss.

Thermocouples of the reactor are connected to available channel for sensors. Unit is switched on and temperatures for all the thermocouples are checked. If the battery backup for the Yokogawa recorder is exhausted, thermocouple reading will be appearing in millivolt. In that case, programs for converting millivolt to ° C, setting the alarm level updating the data and time are given (Ref: Manual for Yokogawa recorder). All the input data are checked by pressing “LIST” button.

Heating is started through TIC-102. It is set to heat up to about 125 ° C in manual mode with current output (OP) of about 20% and then in auto-mode to final temperature corresponding to full design steaming temperature. (Controller is adjusted to deliver maximum 60% current output while heating up in auto mode. This is required to safe guard the heating coils by avoiding rapid increase in temperature of the heating elements).

During heating, nitrogen gas (25±5 cc/min for small) is passed through the reactors in order to fluidize the catalyst to maintain uniform temperature in the catalyst bed. Fluidizing air to the sand bath is started when TIC 102 attains about 200 ° C. The airflow rate is adjusted corresponding to pressure drop of 0.5 kg/cm^2 (g) across the sand bath.

When the final steaming temperature is reached and becomes steady, nitrogen flow is stopped and water is injected by peristaltic pump is started. Pump flow rate is adjusted at (4.0 ± 0.5) ml/hr for small reactors and (180 ± 5) ml/hr for big reactor.

After the required time duration, both furnace heating and water injection is stopped and rectors are allowed to cool down naturally.

Catalyst from steam reactors is unloaded on the next day and stored in a sealed bottle for further analysis. Weight of the recovered catalyst and amount of the water injected is noted in the Auto-Steaming Logbook .

ATTACHMENT –2

COMPUTER STARTUP

Put on the power switches of the panel as well as PC.

Once the computer is switched on, it will automatically enter the software. "OVERVIEW" graphic page will come on the screen automatically. Then press "CONFIGUATION". Configuration graphics page will come.

Enter all the set points, cycle times and temperature tolerance for all the steps of a cycle in the configuration page:

	Purging	Reaction	Stripping	Regeneration	Cooling
PARAMETERS					
TIC-51 SP °C					
TIC-52 SP °C					
TIC-53 SP °C					
TIC-101 SP °C					
TIC-103 SP °C					
TIC-104 SP °C					
TIC-105 SP °C					
TIC-106SP °C					
TIC-71 SP °C	450	450	450	450	
FIC-21A SP CC/min				80	
FIC-21B SP CC/min	30		20		
FIC-21C SP CC/min				40	
CYCLETIME sec	600		900	1200	800
Temp. Tolerance °C	1			1	

Note: ‘.’ indicates specific value for the particular set of experiments;

Press ‘Purging’ to get the purging cycle screen. In this way, status of all the steps of a cycle can be seen by pressing corresponding cycle step, which are located at the bottom of the screen.

Select manual mode by using the ‘A/M’ switch located at the left bottom corner of the screen.

ATTACHMENT NO-3:

CALCULATION PROCEDURE

CALCULATION OF GASEOUS PRODUCTS :

Yield of any gaseous product = (TGV * TCF * (sum of the product of A and D)/W where,

TGV = Total gas Volume in litre

TCF = Temperature correction factor

A_i = Mole % of i^{th} component (from gas analysis)

D_i = Density of i^{th} component, gm/litre

W = Weight of feed injection, gm

i = H_2, C_1, C_2, C_3 (all isomers), C_4 (all isomers) and C_5 .

CALCULATION OF COKE YIELD :

Coke yield (wt %) = ((weight of CO_2) * 12 * 100) / (44 W)

CALCULATION OF LIQUID YIELD:

Yield of any liquid product = (WLP * ALP)/W

Where,

WLP = Weight of liquid collected

ALP = Weight % of respective liquid cut (from liquid analysis)

MATERIAL BALANCE (MB):

= Sum of Gaseous Yield + Coke Yield + Sum of all Liquid Product Yield

CONVERSION:

= Coke Yield + Sum of gaseous Yield + Sum of Liquid products boils up to 216^{0}C

NORMALIZED YIELD PATTERN :

If material balance is not exactly 100, then find out the factor (100/exact MB) and multiple all the yields with this factor.

COKE AND CONVERSION FACTOR :

$$\text{Coke Factor} \quad : \quad \frac{\text{(Coke yield at base W/F for new catalyst)}}{\text{Coke yield at base W/F for base catalyst}}$$

$$\text{Conversion Factor} \quad : \quad \frac{216^0 \text{ Conversion at Base W/F for new catalyst}}{216^0 \text{ Conversion at Base W/F for base catalyst}}$$

DELTA YIELD CALCULATION :

$$\text{Delta (j)} = \frac{\text{Yield (j) at base conversion for new catalyst}}{\text{Yield (j) at base conversion for base catalyst}}$$

Yield (j) = Yield of jth product

ANNEXURE 3:

AUTO MICRO ACTIVITY (AMAT) TEST

INTRODUCTION

Auto Micro -Activity test unit is used to measure the micro - activity of pretreated fresh FCC catalysts / catalyst additives and also to evaluate the crack ability of different FCC feed stocks to get their relative performance with respect to reference catalyst/catalyst additive or reference feedstock. This information is essential for selection of best possible catalyst /catalyst additive or feedstock for any specific FCC operation.

Reactor Cleaning:

Rinse the reactor with acetone or any suitable solvent to remove coke and catalyst particles. Dry the reactor with hot air.

Reactor Loading Procedure

Insert a plug of glass wool (about 6-8 mm. height) into the reactor. Exact height of the glass wool bed can be checked with marked steel rod. Make sure that the bed is inserted horizontally. Load the exact specified amount of steamed, screened by 325 mesh size screen, free of iron, FCC catalyst or a mixture of catalyst and catalyst additive, depending on the specification given by the indentor in the job requisition form, in a free falling manner. Give a gentle vibration to the reactor surface so that catalyst particle adhered to the inner surface of the reactor falls on the catalyst bed. Then holding the reactor vertically

Place it within the furnace; position properly and tight it to leak proof. Place the thermocouple into the reactor through the thermo well to get the bed temperature and cover the reactor top by glass wool to minimize heat losses.

Leak Proof Test

Once the catalyst is loaded in the reactor, pressure test is to be done to get the leak proof system. Pressurize the system at about 90 cm of water column by nitrogen by closing the reactor outlet and inlet valve. Wait for few minutes to ensure that no leakage exists. If leak is exist, locate where the leak is and tight accordingly.

Keep supply of nitrogen and oxygen/air to the unit. Put on the switch of compressor line; make sure there is no condensed water in the compressor.

Once everything discussed above are in order, press the button "start" and allow the system to heat up to the desired value, i.e. in the range of 400 - 600 ° C depending on specific application. Once the start button is pressed the screen will show "reactor to liq. receiver?" Press it. During heating up the system, make sure that 30 ± 5-ml/min. nitrogen is passing through the reactor.

When the reactor temperature reaches the desired value, take the empty weight of clean and dry liquid receiver and connect it with reactor outlet and gas receiver inlet line in such a way that receiver body is immersed in a bath full of ice to maintain nearly zero temperature. Allow the system to be stable for 20 minutes.

After completion of purging operation, fill the syringe with the feed under consideration and then weigh the syringe assembly. Connect the syringe to the reactor feed inlet line. For heavy feed place the tape heater on the feed syringe so that body temperature of the syringe is kept constant at about 80 ° C throughout the feed injection period. However, for lighter feed, this heating is not required because the feed will be in homogeneous condition at room temperature itself.

Check the syringe and reactor bed temperature.

Set syringe size, syringe flow and pump position on feed syringe pump setup to fix the feed injection quantity in order to get conversion at desired severity level.

Bring the syringe drive head in contact with the syringe plunger.

Check the “NEXT STEP” command appears in the screen. Once the command will come and check whether regulator pressure, which control six port valve’s inlet pressure, is minimum 3 kg/cm^2 or , if not, wait till it reach to that pressure.

Allow feed injection by pressing ‘NEXT STEP’. Note down the bed temperature drop during reaction and the amount of gas formed during this period in the Auto MAT operating data logbook. Once the injection is over, system automatically moves to the stripping mode where stripping nitrogen flow rate and duration are fixed as given in attachment no. 2.

After completion of stripping, temperature will start rising to attend regeneration value. During this time remove the liquid receiver and dry it perfectly with the help of tissue paper and if required, heat gently by air dryer to remove the moisture and take the weight of the receiver.

Mix the liquid product with carbon-disulphide (CS_2) solvent homogeneously and sample it. Put the Auto MAT experiment no. e.g. AMAT-2001, on the sample bottle.

Note down the gas volume and mix up the gas properly and sample it in gas sampler. Write down the sample number of gas and liquid in central logbook CED/GC/RGA-SDA/IN/R/2002/01 for analysis.

Once the temperature of the furnace at three different locations as well as the bed are about 660 ± 5^0C,check whether CO_2 and moisture absorbers are required to be change (inspect physically). If required, change it. Connect the reactor outlet to the CO_2 absorption system after taking the weight of two absorbers connected in series.

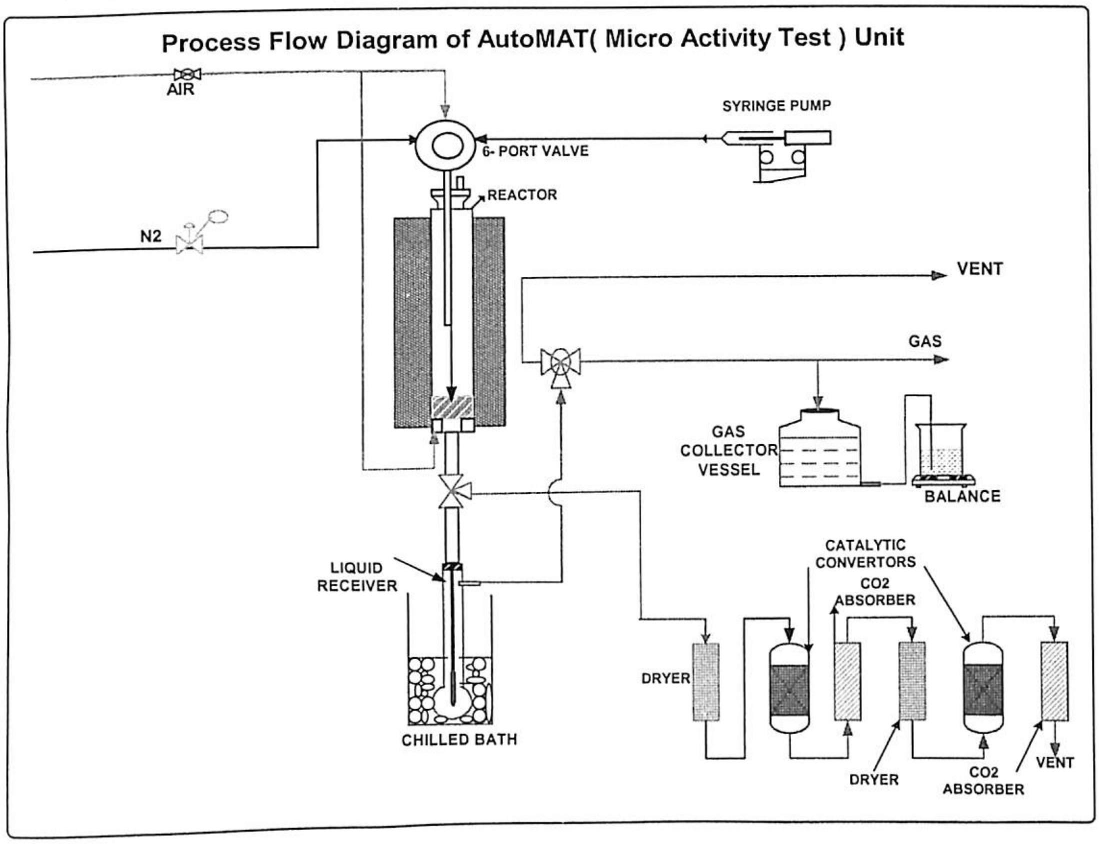
The screen will show the “NEXT STEP”. Press it. By pressing “NEXT STEP”, the regeneration operation will start. Make sure that there is proper supply of oxygen/air.

After completion of regeneration, take weight of CO_2 absorbers.

Allow the reactor to cool down for sometime by allowing cooling air along with nitrogen to flow through the reactor.

Calculation procedure to get material balance as well as yield of different products is indicated in attachment 3.

Repeat the experiment at different severity levels, viz. flow settings of (30,30), (10,10), (10,8) and (5,4) etc. by the combination of syringe size and flow rate setting.



Process Flow Diagram of AutoMAT(Micro Activity Test) Unit

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ANNEXURE 4:

XRD

Zeolite is crystalline in nature and diffraction methods are prime technique for structural characterization. The powder X-ray diffractometer is the primary mean of zeolite phase identification. The appearance of diffraction pattern depends upon the uniformity of the periodicity.

XRD data are also used frequently in measuring sample crystallinity (based on comparison of selected peak heights or areas with those obtained from fully crystalline methods) and unit cell dimensions. The purpose of XRD patterns is to be able to determine the unit cell parameters and thus unit cell volume when the zeolitic structure is known, then one can determine if an element has been introduced into the lattice framework position. It is also a measure of the purity of a compound, compared with reference spectra. If there is no evidence of crystalline or amorphous contaminants present, then one must compare the intensity of the reference with the authentic sample to check for the same composition and crystal size.

However, it is known that zeolite is either orthorhombic or, to a lesser extent, monoclinic.. According to reference materials, small changes in the XRD pattern can indicate the change from a monoclinic to orthorhombic structure, with the loss of the characteristic "doublet" at 24.4 (2 theta) [3]. Meanwhile, peaks at 23.3 and 23.8o also show structural changes of the sorbates, while the crystalline structure remains intact

Surface area

It is indirect measurement of the catalyst activity. Larger the surface area higher the activity under milder or less severe conditions. This measurement is based on surface area found in both small (presumed to be zeolite) and large pores (presumed to be matrix).A loss of surface area indicates a loss of catalytic activity. BET analysis is used to measure the surface area based on nitrogen adsorption isotherm of multimolecular adsorption. This method depends upon the measurement of the volume of gas required to cover the monomolecular layer. Knowing the area covered per molecule the surface area can be calculated.

Methodology for calculating the surface area:

(i)Sample is heated under vacuum for two hours to remove all adsorbed water and volatile compounds.

(ii)The dead space around the sample within the bulb is then determined using helium gas.

(iii)An adsorbed gas such as argon, N2 or krypton is admitted to adsorption bulb at liquid nitrogen temperature in successive increments.

(iv) A plot of the amount of gas adsorbed against the pressure of the adsorbed gas at a fixed temperature is called adsorption isotherm.

(v) The reciprocal of the slope of adsorption isotherm gives the volume of the gas required for monolayer.

(vi) Knowing the cross sectional area of an atom of gas and weight of the sample, the SA can be calculated.