FCC Cracking, Catalyst coking and regeneration, Design concepts, New Designs for Fluidized-Bed Catalytic Cracking Units

- Refining Process and Catalysts,[1,2,21,22]
- Fluid Cracking Catalyst (FCC).
- FCC additives.
- Reforming Catalyst.
- Catalyst Characterization.
- R & D & Commercialization Status in India.
- Conclusion.

**FCC SCENARIO IN INDIA**

- FCC Units in Operation : 15
- Total FCC Capacity ~ 26 MMTPA
- Future FCC Capacity ~ 42 MMTPA

**FCC PROCESS**

![FCC Process Diagram](image)

**Fig: 4.16 FCC PROCESS**

**FCC RISER/REGENERATOR COMBINATION**

![FCC Riser/Reenerator Diagram](image)
Fig: 4.17 FCC/RISER/REGENERATOR COMBINATION

**KELLOG DESIGN RISER UNIT**

Fig: 4.18 KELLOG DESIGN RISER UNIT \[^{[1,2]}\]

**KELLOG RESID FLUID CATALYTIC CRACKING (RFCC)**
Fig: 4.19 KELLOG RESID FLUID CATALYTIC CRACKING (RFCC)\cite{1,2}

ZEOLITE STRUCTURE\cite{3}
**FCC: Some Interesting Facts**

- Nearly 20% of crude is being processed at FCC.
- Larger FCC units holds about 400 Tonnes of catalyst.
- Four major manufactures (Grace Davision, Engelhard, Akzo Nobel, CCIC) supply 1400 tons of catalyst daily to process 12 million barrels per day (600 MMT/day).
- 400 FCC units in world.

**PROCESS VARIABLES**

In addition to the nature of the charge stock, the major operating variables effecting the conversion and product distribution are the cracking temperature, catalyst/oil ratio, space velocity, catalyst type and activity, and recycle ratio. For a better understanding of the process, several terms should be defined.

**Activity**: Ability to crack a gas oil to lower boiling fractions.

**Catalyst/oil ratio (C/O)** \(=\text{lb catalyst/lb feed.}\)

**Conversion** \(=\text{100 (volume of feed volume of cycle stock)/volume of feed.}\)

**Cycle stock**: Portion of catalytic-cracker effluent not converted to naphtha and lighter products [generally the material boiling above 430°F (220°C)].

**Efficiency** \(=(\% \text{ gasoline})\) conversion.

**Recycle ratio** = Volume recycle/volume fresh feed.

**Selectivity**: The ratio of the yield of desirable products to the yield of undesirable products (coke and gas).

**Space velocity**: Space velocity may be defined on either a volume (LHSV) or a weight (WHSV) basis. In a fluidized-bed reactor, the LHSV has little meaning because it is difficult to establish the volume of the bed. The weight of the catalyst in the reactor can be easily determined or calculated from the residence time and C/O ratio.

**LHSV** \(=\text{Liquid hour space velocity in volume feed/(volume catalyst)(hr).}\)

**WHSV** \(=(\text{Weight hour space velocity in lb feed)/(lb catalyst) (hr).}\)

**Within the limits of normal operations, increasing**\(^{[1,2,23]}\)

1. Reaction temperature
2. Catalyst/oil ratio
3. Catalyst activity
4. Contact time

Results in an increase in conversion, while a decrease in space velocity increases conversion. It should be noted that an increase in conversion does not necessarily mean an increase in gasoline yield, as an increase in temperature above a certain level can increase conversion, coke and gas yields, and octane number of the gasoline but decrease gasoline...
yield. In many FCC units, conversion and capacity are limited by the regenerator coke burning ability. This limitation can be due to either air compression limitations or to the after burning temperatures in the last stage regenerator cyclones. In either case FCC units are generally operated at the maximum practical regenerator temperature with the reactor temperature and throughput ratio selected to minimize the secondary cracking of gasoline to gas and coke. With the trend to heavier feedstocks, the carbon forming potential of catalytic cracker feeds is increasing, and some units limited in carbon burning ability because of limited blower capacity are adding oxygen to the air to the regenerator to overcome this limitation. Oxygen contents of the gases to the regenerator are being increased to 24–30% by volume and are limited by regenerator temperature capability and heat removal capacity.

**GROWTH OF CATALYSTS IN FCC**

![Growth of catalysts in FCC](image)

**Reactions in FCC**

- Paraffins are cracked to give olefins and smaller paraffins.
- Olefins are cracked to give smaller olefins.
- Napthenes (cycloparaffins) are cracked to olefins.
- Alkyl aromatics lose their side chains.
- Isomerisation of olefins to iso-olefins.
- H-transfer reactions.

**Acidity of solid catalysts**
FCC Catalyst

Catalyst Components
Zeolite
Matrix
Binder
Filler

FCC Catalyst preparation

Non-Wash route
Wash route

Structure of Zeolite[23]
**Fig:4.22 Structure of Zeolite**

**Zeolite**

![Zeolite Preparation Diagram](image)

**Fig:4.23 Zeolite**

**Further treatments of NaY zeolite**

- Ion Exchange.
- RE Exchange.

**Preparation methods of High-Silica Y zeolites**

- Thermal and hydrothermal modification.
- Chemical modification.
- Combination of hydrothermal and chemical modification.

**Ion Exchange**

\[
\begin{align*}
\text{Ammonium Exchange} & : \quad \text{Na}^+ - \text{Z}^+ + \text{NH}_4^+ \xrightarrow{\text{Calcination}} \text{Na}^+ + \text{NH}_4^+ - \text{Z}^+ \\
\text{Rare Earth Exchange} & : \quad 3\text{Na}^+ - \text{Z}^+ + \text{RE(H_2O)_x}^{3+} \xrightarrow{\text{Hydrolysis}} 3\text{Na}^+ + \text{RE(H_2O)_x}^{3+} - \text{[Z]_3}^3 \\
\end{align*}
\]

**Thermal and hydrothermal modification**
1. Introduction

The word 'Zeolite' is derived from the Greek word, which means 'boiling stone' (2002). Zeolites are water-containing crystalline aluminosilicates with highly ordered structures. They can be of naturally originated or synthesized and consist of SiO₄ and AlO₄- tetrahedra. These tetrahedras are interlinked through common oxygen atoms to give a three-dimensional network through which long channels run (2006).

A representative empirical formula for a zeolite can be written as \( M_{x/n} \left[ (AlO_2)^x (SiO_2)_y \right] mH_2O \). Where, M is the cation of valency \( n \); \( x \) and \( y \) represents Si/Al ratio and having value from 1 to 8. When M cations are replaced by \( H^+ \) ions, the active catalysts can be generated and used in the petroleum industries for cracking, hydrocracking and isomerization reactions (1982). Zeolites provide excellent shape selectivity and acidic sites. Due to these characteristics, zeolites have dominant applications in petroleum industries.
Hydrocracking and hydroisomerization are the two of the most important processes of the petroleum refineries, which are not possible without application of suitable catalysts (Fig.4.26). The continuous increase in global demand of the petroleum products increases the valuation of these processes in modern refineries. Hydroisomerization is termed as the isomerization of n-paraffins into branched isomers. Hydroisomerization of C₄–C₇ hydrocarbons has been applied for the production of gasoline with a high octane number. Hydroisomerization of C₇ –C₁₅ paraffins applies to improve diesel fuel cold flow properties, such as viscosity, pour point and freezing point. The hydroisomerization reaction is always accompanied by a hydrocracking reaction that lowers more or less the yield of that the isomerized feed molecules[27] (2005).

Catalysts used for hydroisomerization reactions are bifunctional in nature. They generally contain metal such as Pt, Pd, Ni etc. dispersed on acidic supports. While hydroisomerization and hydrocracking reactions, metals are responsible for hydrogenation-dehydrogenation agent and acidic supports are responsible for isomerization and cracking of the substances[28] (2003). Zeolite acidity (number and strength distribution) and pore structure play important role in overall reactions.

Typical acidic supports of bifunctional catalysts used are amorphous oxides or mixture of oxides (i.e. HF-treated Al₂O₃, SiO₂–Al₂O₃, ZrO₂/SO₄²⁻); zeolites (Y, Beta, Mordenite, ZSM-5, ZSM-22, ZSM-12 etc.); silicoaluminophosphates (SAPO-11, SAPO-31, SAPO-41) and mesoporous materials (MCM-41, AIMCM-41) (Deldari, 2005).

Gasoline and diesel are the most important and valuable fractions generated by petroleum refineries. The demand of these two fractions have globally increased since last few years. The average demand for diesel will be almost twice than that of the demand of gasoline in next few years (Fig.4.27). So, major part of the investments of the petroleum refineries have covered processes for production or upgrading of middle distillate fractions to make them suitable for diesel blendstock[29] (2010).

So, objective of this work is to develop suitable molecular sieve based catalysts for the hydroisomerization of middle distillate fractions. The catalyst should provide transition shape selectivity for branched isomers. Also, the catalyst should provide good mechanical strength during reaction conditions and structure (especially in the case of molecular sieves) should not collapse at reaction conditions. The zeolite molecular sieves successfully fulfilled all these criterions and have been commercially used since their invention. Therefore, development of the noble metal (i.e. Pt, Pd etc.) loaded zeolite (i.e. ZSM-12, ZSM-22, ZSM-48) supported catalysts, is the major objective. Also, development of kinetic model for hydroisomerization followed by hydrocracking reactions will also be performed.
Fig: 4.26 Schematic flow diagram of a modern refinery \[^{[29]}\](2010)

Fig: 4.27 Incremental transportation fuel demand from 2008 to 2015 \[^{[29]}\](2010)
2.1 Introduction to molecular sieves and zeolites (Szostak, 1989)

In 1932, McBain proposed the term "Molecular Sieve" for the materials which have selective adsorption properties and these materials separate components of a mixture on the basis of difference in molecular size and shape. The different classes of molecular sieves are listed in Fig.4.28 Structure of many of these materials are analogous, but all are different in terms of elemental composition and aluminosilicates have been given the classical name 'Zeolites'. Structurally zeolites are the crystalline aluminosilicates with a framework based on an extensive three-dimensional network of oxygen ions. The $\text{AlO}_2^-$ tetrahedra in the structure determine the framework charge and is balanced by cations, which occupy non-framework positions. The crystalline framework structure contains voids and channels of discrete size. The pore opening ranges from 3 to 8Å. The negative charge has been created by $\text{AlO}_2^-$ tetrahedra and balanced by cations like alkaline ($\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$, $\text{Cs}^+$), alkaline earth ($\text{Mg}^{+2}$, $\text{Ca}^{+2}$), $\text{NH}_4^+$, $\text{H}_3\text{O}^+$ ($\text{H}^+$), $\text{TMA}^+$ (Tetramethylammonium), other nitrogen containing organic cations, and rare-earth and noble metal ions. All aluminosilicates are molecular sieves but not zeolites. An aluminosilicate is called zeolite if it contains at least one aluminium ion per unit cell based on the bulk composition of the sample, with no allowance made for inhomogeneities within the individual crystal on the microscopic level.

![Molecular Sieves](image)

**Fig:4.28 Classification of molecular sieve materials indicating the extensive variation in composition**[30](1989)

**Fig:4.29 Examples of pore opening in the zeolite molecular sieves**[25](2006)

Zeolites have been classified on the basis of different structural elements. The kind of building unit most suitable for the classification of the zeolites depends on the property under consideration. If we are able to identify ability of a particular zeolite to selectively adsorb one component of a mixture over another, understanding of the detailed complex structure of that particular zeolite would not be necessary. Size of the pore opening of the particular zeolite is responsible for selective adsorption of particular components. So, we can classify zeolite from on the basis of pore size to sequence of building blocks which form the regular network pattern characteristic of the zeolite. Each level acts as a model to understand, describe or visualize a specific aspect of a material.

The first level of classification is based on pore size. All the zeolites used for catalytic or adsorption operations can be
A typical hydrothermal zeolite synthesis can be described in brief as follows:

- Silica and alumina sources in the amorphous form have been mixed together in the alkaline pH and in an aqueous medium with a cation source.
- The reaction mixture has been heated in a sealed autoclave at temperature above 100°C and autogeneous pressure.
- After reaching the appropriate temperature, reactants remain amorphous for some time and this time is known as "induction period". Crystallization starts after this period of time.
- After appropriate time period, all the amorphous materials will be converted into zeolite crystals. These crystals are recovered by filtration, washing and drying.

The Si and Al sources have been used in an oxide form and these amorphous precursors contain Si-O and Al-O bonds. At the end of the hydrothermal synthesis crystalline zeolite products containing Si-O-Al linkages has been created in the presence of "mineralizing" agent (generally alkali metal hydroxide). The bond type of the product is very similar to the bond types of precursor oxides. So, it can be concluded that, no great enthalpy changes has been takes place. In fact,
overall free energy change of the reaction is small enough to become the overall reaction kinetically controlled. This gives the benefit of generation of metastable products. To make the synthesis process industrially important, the product must contain reproducibility and the same specification each time. This needs to develop exact conditions for product optimization. This influences the choice of starting reagents from wide varieties of simple oxides or hydroxides to sodium silicate solution and solid sodium aluminate. Usage of sodium silicate solution or solid sodium aluminate gives not only benefits in terms of cost or ease of operation but also they offer optimum routes to particular materials. Flexibility in the choice of reagents enables equilibria to be approached from various directions. We may also get the kinetic benefits like preferred nucleation of one phase over another in the situations of possibility of co-crystallization of the materials.

Now let’s come to the synthesis mechanism for zeolites. The most probable pathways can be given as induction period, nucleation and crystal growth in sequence. Induction period is the time (t) between the notional start of the reaction and the point at which the first crystal formation can be observed. According to the classical nucleation theory, the induction period has been divided into three subunits as relaxation time ($t_r$), time for formation of stable nucleus ($t_n$) and time for the nucleus to grow to a detectable size ($t_g$). ‘Nucleation’ is defined as the series of atomic or molecular processes by which the atoms or molecules of a reactant phase rearrange into a cluster of the product phase large enough as to have the ability to grow irreversibly to a macroscopically larger size. The ‘cluster’ is defined as nucleus or critical nuclei. The rate of nucleation (i.e., the number of nuclei formed per unit time per unit volume) can be expressed by an Arrhenius-type equation \((29)\) (2010):

\[
J = A \exp \left(\frac{-\Delta G^*}{kT}\right)
\]

Where, $\Delta G^*$ is the critical Gibb’s free energy, $k$ is rate constant at temperature $T$. Cations and organic-structure-directing agents also involved in the nucleation process by surrounding themselves with metal-oxide species in preferred geometries. Crystal growth is considered as one of the most important step and studies tell that zeolite growth increases linearly during most of the crystallization process for both gel and clear solution synthesis. Temperature, gel composition, agitation and aging are the various parameters which affect the zeolite growth \((29)\) (2010).

### 2.3 Characterization of zeolites

Characterization of the synthesized zeolites is very important aspect. A particular zeolite must contain good crystal structure, required Si/Al ratio, desired BET surface area and pore size, desired acidic and metal sites, good dispersion of metal sites, proper crystal morphology etc. for particular application. Each of the above mentioned properties can be verified by various characterization techniques like X-Ray Diffraction (XRD), BET surface area analyzer, Solid state Nuclear Magnetic Resonance (Solid NMR), NH$_3$ or Pyridine Temperature Programmed Reduction (NH$_3$ -TPD or Pyridine-TPD), H$_2$ -Chemisorption or CO-Chemisorption, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) (both normal and high resolution) etc.

### 2.4 Classification of zeolites

Zeolites are comprehensively classified on the basis of their morphology, crystal structure, Chemical composition, effective pore diameter, origin of trivalent species donor.

#### 2.4.1 Morphology

Fibrous: Tetrahedra linked more numerous in one crystallographic .Lamellar (Open framework): Tetrahedral linkages within similar plane. Zeolites have been structurally classified on the basis of Secondary Building Unit (SBU). They can be explained as cage or ring like structures which forms the basic architecture of zeolites. Fig.4.33 shows some of the SBU.

#### 4.33 SBU in zeolite skeleton.

#### 2.4.2 Unit cell size:

It is an elementary building block of the zeolite crystal.

$N_{Si} + N_{Al} = 192$

Al/Unit cell= 111.52 (UCS – 24.191) developed by Breck and Flannigan.

<table>
<thead>
<tr>
<th>cell</th>
<th>UCS(Å)</th>
<th>Al/Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY (As synthesized)</td>
<td>24.64 – 24.67</td>
<td>54</td>
</tr>
<tr>
<td>USY</td>
<td>24.50 – 24.54</td>
<td>40</td>
</tr>
<tr>
<td>Equilibrated USY</td>
<td>24.25 – 24.30</td>
<td>2 - 13</td>
</tr>
</tbody>
</table>
2.4.3 Rare earth level:

Rare earth elements serve as a bridge to stabilize aluminium atoms in the zeolite structure.

<table>
<thead>
<tr>
<th>Rare earth exchanged</th>
<th>zeolite(°A)</th>
<th>USY</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>UCS</td>
<td>Low</td>
</tr>
<tr>
<td>High</td>
<td>Zeolite activity</td>
<td>Low</td>
</tr>
<tr>
<td>High</td>
<td>Gasoline selectivity</td>
<td>Low</td>
</tr>
<tr>
<td>Low</td>
<td>RON</td>
<td>High</td>
</tr>
<tr>
<td>High</td>
<td>Hydrogen transfer</td>
<td>Low</td>
</tr>
<tr>
<td>High</td>
<td>Hydrothermal stability</td>
<td>Medium</td>
</tr>
</tbody>
</table>

2.4.4 Chemical Constitution

Zeilotes are classified on the basis of their framework silicon and aluminum constitution. This classification is mainly done on the basis of the Silicon to Aluminum ratio and was introduced by Flanigen[32] (1982). Table 1 vividly describes some of the zeolites.

Tab: 4.5 Silica rich and poor zeolites.

<table>
<thead>
<tr>
<th>Pure Silica Zeolites</th>
<th>Si/Al = 8</th>
<th>Si-MEL (silicalite-2), Si-MFI (silicalite-1), Si-FER etc</th>
<th>High Silica Zeolites</th>
<th>Si/Al = 5-500</th>
<th>MFI, BEA, FER etc.</th>
<th>Intermediate Silica Zeolites</th>
<th>Si/Al = 2-5</th>
<th>Erionite, Chabazite, MOR, L, X, Y etc.</th>
<th>Low Silica Zeolites</th>
<th>Si/Al = 1-1.5</th>
<th>A, X, Sodalite, etc.</th>
</tr>
</thead>
</table>

2.4.5 Pore Size Diameter

Different zeolites have different opening ring combination. Such as Fig.4.34 a) displays the graphical view of MFI zeolite with 10 Member Ring (M.R.) opening structure. While Fig.4.34 b) displays dimensions of LTA zeolite with 8 M.R. Structure. Fig.4.34 c) elaborates dimensions of VPI-5 with 18 M.R. Some examples of different zeolites containing.

Fig:4.34 Ring opening structures along [001] of some zeolites. (Units mentioned in fig are in Angstrom unit)

Tab 4.6 Classification based on ring opening

<table>
<thead>
<tr>
<th>Small Pore 8 M.R.</th>
<th>Medium Pore 10 M.R.</th>
<th>Medium Pore 12, 14 M.R.</th>
<th>Large Pore 18, 20 M.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chabazite</td>
<td>MOR</td>
<td>CIT-5 (14)</td>
<td>VPI-5 (18)</td>
</tr>
<tr>
<td>Erionite</td>
<td>VPI-8</td>
<td>UTD-1F (14)</td>
<td>Cloverite (20)</td>
</tr>
<tr>
<td>LTA</td>
<td>ZSM-22</td>
<td>A IPO-5 (12)</td>
<td></td>
</tr>
<tr>
<td>ITQ-3</td>
<td>ZSM-18</td>
<td>ZSM-12 (12)</td>
<td></td>
</tr>
</tbody>
</table>

2.5 Characteristics and Physicochemical properties of zeolites (Deldari, 2005)

Global rise in demand of zeolites can be justified with the help of some following properties of zeolites followed by discussing the chief properties of zeolites. High surface area, uniform micropore size, high hydro thermal stability, intrinsic acidity, ability to accommodate active metal species, introducing constraints to undesired species by molecular sieving effect (shape selectivity), environmentally harmless, non-corrosive, show ease of separation from reaction mixture compared with homogeneous catalysts.

2.5.1 Framework Cation Exchange

The zeolite framework is comprised of Silicon and Aluminum linked together with oxygen atoms to form tetrahedra. To stabilize the structure or to compensate negative charge imparted by aluminum due to its valency, a cation is required. Cation exchange properties of zeolite is function of its intrinsic properties like (i) Framework topology (ii) Ion size and shape (iii) Charge density of anionic framework (iv) Ion valence (v) Electrolyte concentration in aq. Phases.

2.5.2 Size Constraints or Molecular sieving or Shape selectivity

Due to rigid skeletal system, zeolite window has intact window size due to which molecules having size larger than this window dimensions often experience constraints in accessing the intrinsic sites. Thus, prevents undesired large molecules to enter network. Depending upon this shape selectivity is being classified into three main subdivisions as described in brief below.

2.5.2.1 Reactant Shape selectivity

This refines the accessibility molecules inside pore geometry of zeolite by imparting the fixed window opening, thus limits the diffusion of molecules with kinetic diameter larger than this window. This allows shape selective entrance of molecules, activity of such molecules is often hindered. Fig.4.36 shows the shape selectivity of n- butane and iso-butane over zeolites.

4.36 Shape selectivity of hydrocarbon reactants on to zeolite framework.

2.5.2.2 Transition Shape selectivity

Transition shape selectivity refers to curbing of intermediate compounds formed therein the framework whose size is larger than skeleton size. Fig.4.37 shows formation of small sized isomer compared to bulky ones.

4.37 Shape selective transition compound formation restriction.

2.5.2.3 Product Selectivity

Due to restricted pore size products diffusing through these materials experience constraints and so product formed is also selective in nature. But however sometimes this bulky products accumulate over a position of zeolite blocking the accessibility of virgin molecules resulting into coking or deactivation of catalyst.

4.38 Shape selective product formation

2.5.2.4 Molecular Traffic Control

In case of some selected zeolites, having multi dimensional channels, in such cases reactants access pores other than what product diffuse out. This becomes easier as counter diffusion is prevented. Several probing techniques are investigated for having clear idea on shape selectivity of zeolites amongst which some includes: (i) Constraint Index (ii) Refined constraint index (iii) Spacious Index, o-p index.

2.6 Applications of zeolites

2.6.1 Ion-exchange

Natural zeolites have a very gifted tendency to ion exchange some water pollutants. Clinoptilolite is successfully employed for removing Ammonium from municipal sewages. Regeneration is performed by NaCl and CaCl\textsubscript{2}. Ammonia is air stripped in regeneration and absorbed by sulphuric acid to give ammonium sulphate, a kind of fertilizer. An advantage of zeolites for elevated resistance compared to organic resins for wastewaters of nuclear industry has been investigated.

2.6.2 Agricultural Uses

Soils of volcanic origin are prone to have some fraction of natural zeolites, so they give some indications for their application in improving soil fertility. Natural zeolites helped many plants including spinach, radish, sugar beet, tomato, maize, rice, potato and cucumber[33] (2011).

2.6.3 Adsorption
The simplest is to reduce the backend cutpoint and add kerosene blendstock. This action removes the heavier paraffinic molecules that tend to precipitate at higher temperatures. However, reduction of the end point results in significant reduction of diesel yield from the crude.

- Removal of wax-forming components by crystallization after dilution of the feedstock with a suitable solvent and chilling (i.e., solvent dewaxing). This option is generally economical only for feedstocks with a high content of paraffins, and it is mainly used for the production of lubricating oil base stocks.

- Usage of cold-weather additives to meet seasonal low-temperature.

- Catalytic dewaxing process wherein the waxy paraffin are selectively cracked or isomerized.

All of above mentioned techniques; catalytic dewaxing process is of our interest. Catalytic dewaxing is a process where the products are removed which are responsible for the degradation of the cold-flow properties. They are removed by selective cracking to lighter compounds, by boiling in the gasoline and LPG range (i.e., cracking dewaxing), or by isomerization into more branched lower melting point structures minimizing as much as possible the cracking (i.e., isomerising dewaxing).

The detailed mechanism of the hydrosisomerization and hydrocracking of n-alkanes on bifunctional catalysts is shown in Fig.4.39


A catalyst can be used for hydrosisomerization, if it contains following properties [27](2005):

- It should provide good selectivity of isomerized products.
- It should have proper balance of acidic and metal sites.
- It should be able to withstand high pressure and temperature.
- The pore opening of the catalyst is small enough to restrict the larger isoparaffins from reacting at the acidic sites.

The term cold-flow properties refer to the flow characteristics of a diesel fuel after at low temperature range. If cold-flow properties don’t change with respect to temperature, it is termed as good. It is the ability to operate under cold weather conditions. Petroleum products contain different hydrocarbons like n-paraffins, i-paraffins, olefins, naphthenes, and aromatics. Among these, normal and slightly branched paraffins have relatively high melting points in the typical range of 250–360 °C. The melting point of normal paraffins ranges between 10 and 40 °C, while the melting point of the heaviest methyl paraffin present (C_{21}) is, depending on the position of the branching, between –4 and 13 °C. The extent of decrease in the melting point significantly depends on the degree, the position, and the length of the branching. Branching positions in the middle of the chain have a higher effect than those near the end of the chain, while longer side chains lead to a higher decrease of melting point.

Engines running on diesel should be able to operate even in cold weather conditions where temperature can reach values well below 0°C. On the basis of the data presented above it is evident that such temperatures may cause the crystallization of those compounds presenting the highest melting points, thereby affecting the flow characteristics, and ultimately may lead to solidification of the product. Standard test methods for determining these properties are cloud point (CP; ASTM D2500), pour point (PP; ASTM D97), and cold filter plugging point (CFPP; IP 309). The CP is the temperature at which a haze of wax crystals is formed; PP is the highest temperature at which the product still flows, while CFPP is the highest temperature at which the wax crystals severely reduce the flow through a filter. Different options are available to improve the cold-flow properties of gas oil:

- It should provide good selectivity of isomerized products.
- It should have proper balance of acidic and metal sites.
- It should be able to withstand high pressure and temperature.
- The pore opening of the catalyst is small enough to restrict the larger isoparaffins from reacting at the acidic sites.

http://nptel.ac.in/courses/103102022/thermal%20and%20catalytic%20cracking/FCC%20Catalytic%20Cracking/coking%20and%20regeneration%20design...
inside the pore.

2.6.5 Matrix

- Physical functions
  - Binder
  - Diffusivity
  - Diluting medium
  - Sodium sink
  - Heat transfer

Manufacturing

4.40 Main Reactions in FCC Catalysis

FCC Catalyst

4.41 FCC Catalyst

ROLE OF ADDITIVES

4.42 Role of Additives

FCC Additives

4.43 FCC Additives

ZSM-5 additive

- Octane boosting.
- Increase in C₃ and C₄ olefins and LPG maximization.
- Preference for higher butylene yield.
- Initially ZSM-5 cracks paraffins and olefins. As cycle time increases, olefin isomerisation dominates while gasoline...
loss and octane improvement is minimum.

Fig 4.44 A typical flow sheet for higher molecular hydrocarbons (feed) cracking with ZSM-5 towards propylene and butylenes.

How to Maximize Propylene Yield?

Fig 4.45 A typical flow sheet for higher molecular hydrocarbons (feed) cracking with ZSM-5 towards lighter olefins, napthenes, paraffins and aromatics.

Cracking by ZSM-5 favored by:[23]

- Low pressure
- High Temperature
- Fast diffusion of primary cracking product from the catalyst.

Secondary catalyst reactions

- Hi-transfer, isomerization, cyclization favored by:
  - High host catalyst ZM
  - High zeolite acid strength, high UCS.
  - Slow diffusion of primary cracking product from the catalyst.

Suppressing competitions from secondary reaction is the major key for maximizing propylene.

Hydrogen Transfer Index

The relative activity of the host FCC catalyst for secondary reactions can be quantified using the Hydrogen Transfer Index (HTI):

Designing a Max C3= Catalyst for Resid[23]

REQUIREMENTS:

- Minimize Hydrogen Transfer to increase C3= plateau.
- Vanadium tolerance for good hydrothermal stability.
- Good bottoms cracking ability.
- Low coke selectivity.
- High accessibility reduces HTI. Primary cracking products can diffuse from the catalyst faster and are less likely to undergo secondary reactions.

Balance between HTI and Activity

- Low Hydrogen Transfer maximizes propylene.
- If achieved by reducing Rare Earth, activity is lower.
- There is a limit to how much zeolite can be used in catalyst to compensate for activity loss.
- Dilution effects from large amounts of ZSM-5 must also be overcome.
- The challenge, particularly for Resid, is achieving high propylene yield AND good conversion with acceptable catalyst addition rate.

Vanadium

- At regenerator conditions, Vanadium on equilibrium catalyst exists as V^{+5}.
- In the regenerator ‘V’ presented on the catalyst converted Vanadium pentoxide (V_2O_5).
- Under regenerator conditions V_2O_5 is mobile because it melts at regenerator conditions.
- In the presence of steam V_2O_5 is converted to Vanadic acid H_3VO_4.

Ni passivators

- ‘Ni’ passivating agents are antimony, bismuth and rare earth compounds (Ce, La, etc...).
- Antimony: This is a first commercially used additive. Ni-Sb alloys formed.
  1. Antimony will block ‘Ni’ active sites.
  2. Alternation of electronic and chemisorption properties.
  3. The amount of antimony available to passivate nickel will be determined by the equilibrium between antimony
and nickel.

**Draw back:** Antimony effects on CO combustion promoters.

**Vanadium Passivators**[^1,2,23]

Vanadium passivating agents are Tin, Titanium, Zirconium and rare earth compounds.

Other than the above stated passivating agents there are other passivating agents are also reported. They are germanium, gallium, indium, tellurium, aluminium, barium, zinc, boron, phosphorous, tungsten, tantalum, lithium and cadmium.

**Metal traps**

Metal traps are added to the FCC Catalyst as separate particle or incorporated directly into the catalyst particle.

These metal traps react with incoming metals like nickel and vanadium and form an inert compounds.

**Fig 4.46 A typical FCC flow sheet in petroleum refining system which incorporates an FCC to distill high-octane gasoline and LPG from the heavy contents of the crude oil with sulphur**

**Catalyst/Additives for Sulphur Control**

- **Grace**
  - GSR Technology for sulphur reduction 15-25%
  - Sulphur reduction is achieved mainly from front end.
  - For Gasoline.

- **AKZO**
  - Resolve FCC catalyst selective matrix activity
  - 15-30% Sulphur reduction.
  - Optimized access.
  - For Gasoline.

- **BCA Additive**
  - 20-30% achieved pesovskite /Spinel.
  - Alumina Matrix.
  - Sulphur capture by Matrix.

**References**