

**Fluidized Catalytic Cracker Catalyst Selection:
Equilibrium Catalyst Quality and Considerations
for Selections**

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Abstract

This article reviews Fluidized Catalytic Cracking Unit;

1. History
2. Process Overview
3. Process Chemistry -Feedstock, Reaction, Catalyst
4. Process Variables
5. Advance in Cat Development
6. Catalyst Evaluation Techniques

To assist refiner's in catalyst selection.

Catalytic Cracking

The technology to convert atmospheric and vacuum tower gas oils, coker gas oils, residual oil, and aromatics lube extracts by fluidized catalytic cracking to gasoline, light olefins and light cycle oil.

Introduction

The objective of Catalytic Cracking is to convert hydrocarbons in the middle distillate range and above (C_{11+}) into the naphtha range ($<C_{12}$), yielding gasoline, heating oil and petrochemical feed stocks.

History of Catalytic Cracking

As early as 1912 thermal cracking was beginning. In 1915 a first attempt of catalytic cracking with aluminum chloride by McAfee – Gulf. In 1936 Houdry – Mobil developed a fixed bed with natural clays. In 1939 the development of fluid bed concepts by Lewis – Exxon. In 1940 Exxon produced the first synthetic silica alumina.

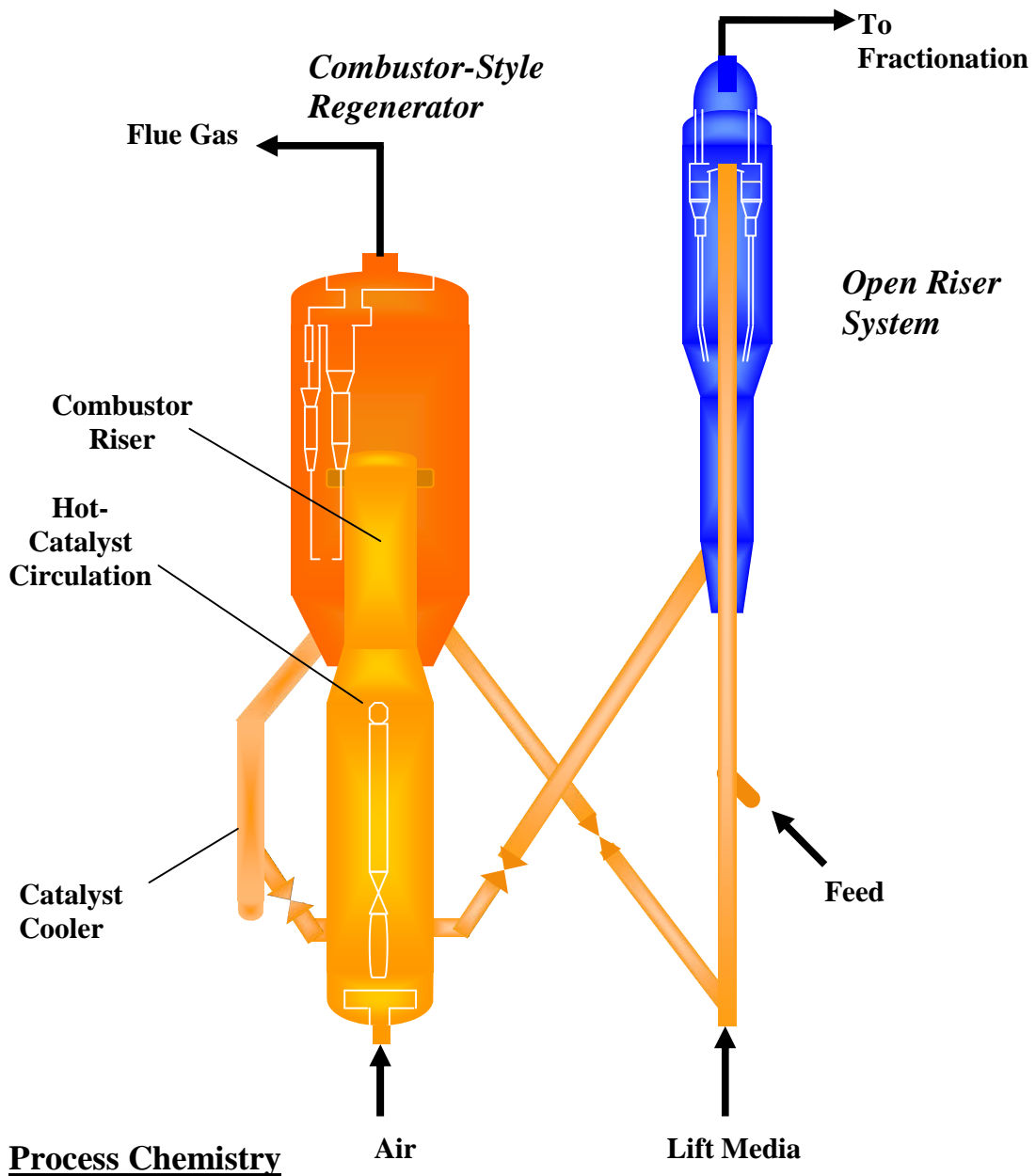
In 1942 Exxon developed the first commercial FCC and Mobil developed the first FCC moving bed. In 1954 Union Carbide developed the synthesis of zeolites. In 1962 zeolites were introduced into the FCC.

In 1971 short contact risers were introduced and 1986 ZSM-5 was added by Mobil.

Process Overview

Reactor Overview

FCC CATALYTIC CRACKING PROCESS



Feedstock Chemistry

Typical FCC Feedstock include:

1. Atmospheric Gas Oils
2. Vacuum Gas Oils
3. Vacuum Tower Bottoms (Resids)
 - A. Raw
 - B. Hydrotreated (HDS)
 - C. Deasphalted (DAO)
4. Coker Gas Oils
5. Lube Extracts
6. Slop Oils

Typical Hydrocracking Feedstock Chemistry

Source	Carbon Number	Boiling Range Degree F / C	Metals ppm	Special Features
Straight Run Naphtha	C5 – C11	/ 70-170		To increase aromatics
SR Gas Oil	C11 - C19			
DAO Resid	C11 – C19		< 200	Low metals and asphaltenes
Recycle Gas Oil	C16 – C25			Higher aromatics
Coker Gas Oil	C16 – C25			Higher olefins and aromatics
Vacuum Gas Oil	C16 – C40	/ 350 – 550		Higher metals and asphaltenes
Vacuum Residua	C40+			Higher metals and asphaltenes
Atm Residua	C40+	/ > 500	> 200	Higher metals and asphaltenes

The exact composition and structure of the feedstock depends on the boiling range, but each stock consist of different amount of:

Typical Hydrocracking Feed / Products

Compound	Gases	Gasoline	Coke
Paraffins	High	Low	Low
Naphthenes	Low	High	Intermediate
Aromatics	Low	Intermediate	High

Feedstock impurities are sulfur, oxygen, nitrogen and metals, which can be lowered by hydrotreating.

Feedstock impurities typically are;

1. Sulfur (0-7.5%)
2. Oxygen (0-2%)
3. Nitrogen (0-0.9%)
4. Metals (0-200 ppm)

Typical Hydrocracking Feedstock Chemistry

Feed	Paraffinic	Naphthenic	Aromatic	Use
Paraffins	80	54	21	
Naphthenes	15	33	8	
Aromatics	15	13	71	
Products Wt%				
H2, C1,C2,C3	5	6	3	Fuels
C2=,C3=, C4=	16	15	3	Chemical Feed stocks, Alkylation
I-C4	6	3	1	Alkylation
N-C4	2	1	0	Chemical Feed Stocks
Gasoline	31	27	23	Sales
Kerosene	3	4	6	Sales
Fuel Oil	21	32	45	Sales
Heavy Oil	6	9	12	Recycle
Coke	5	2	5	Heat, CO, CO2

Reaction Chemistry

The Catalyst is designed to improve the desired activities of hydro cracking, isomerization, alkyl group transfer, and hydrogen transfer, while reducing the unwanted activities of dehydrogenation, condensation and coke formation.

The following main reactions occur:

Typical Hydrocracking Reactions

Reaction Type	Equilibrium	Reaction Enthalpy
Cracking	No	Endothermic
Isomerization	Yes	Almost none
Alkyl group transfer	Yes	Almost none
Dehydrogenation	Yes	Endothermic
Hydrogen transfer	No	Exothermic
Condensation	Yes	Endothermic
Coke formation	No	Endothermic
Alkylation	Does not occur	
Hydrogenation of Aromatics	Does not occur	
Polymerization of olefins	Does not occur	
Methylation	Does not occur	

Hydrocracking

The cracking ease of various hydrocarbons is as follows:

Hydrocarbon	Mode	Products
Olefins	Chain Rupture	Olefins / Paraffins
Alkyl Aromatics	De-alkylation	Olefins / Paraffins
Naphthenes	Chain Rupture	Olefins / Paraffins
Aromatics	None	

The rate of hydrocracking is increased by:

1. Increasing molecular weight
2. Tertiary hydrogen
3. Double Bonds
4. Alkyls on aromatics

Qualitative Observations

1. Cracked fragments contain 3 or more carbon atoms
2. More than two fragments are often produced
3. Methyl groups are not easily removed
4. Carbon rearrangement often takes place

Isomerization

Isomerization can occur as double bond shift and chain breaking

Hydrocarbon	Mode	Products
Olefins	Very Fast	Olefins
Paraffins	None	Paraffins
Naphthenes	None	Naphthenes
Aromatics	Slow	Aromatics

Alkyl Group Transfer

Alkyl Group Transfer mostly involves methyl groups and is a slow reaction.

Dehydrogenation

Little or no dehydrogenation is reacted on the fresh catalyst. It is catalyzed by Ni, FE and V contamination that builds up on the equilibrium catalyst.

Hydrogen Transfer

Hydrogen Transfer is between naphthenes and olefins to produce iso-paraffins and aromatics. A second hydrogen transfer can be olefin to olefin to produce paraffins and coke.

1. Naphthenes + olefin = iso-paraffins + aromatics
2. Olefin + olefin = paraffin + coke

Condensation

Condensation is the formation of higher molecular weight hydrocarbons.
The rate order for condensation is:

Aromatics > Olefins > Paraffins

Condensation is a precursor to coke formation.

Coke Formation

There are four types of coke identified in Catalytic Cracking. Coke can be defined as $\text{CH}_{0.3-1.0}$.

1. Catalytic Coke – from condensation and dehydrogenation, which is about 45% of the coke formed.
2. Cat to Oil Coke – hydrocarbons entrained in the small pores and not removed by the stripper, which is about 20% of the coke formed
3. Conradson Coke – already in the feed, which is about 5%
4. Contaminated Coke – from dehydrogenation catalyzed by Ni, Fe, and V, which is about 30%

Catalytic FCC Reactions

1. C3s are lightest product due to secondary or tertiary positions in the carbonium ion.
2. Olefins are primary products made from:
 - A. Paraffin Cracking
 - B. Naphthene Cracking
 - C. Dealkylation of aromatics or naphthenes
3. Aromatics are produced by naphthene dehydrogenation
4. Larger molecules are more reactive
5. Pure aromatics do not react
6. Paraffins are produced by hydrogen transfer
7. Some isomerization occurs

Thermal FCC Reactions

1. High production of C1 and C2
2. Olefins are less branched
3. Some Di-olefins made at high reactor temperatures
4. Gasoline selectivity is poor
5. Gas and Coke are major products
6. Reactions are slow compared to catalytic reactions