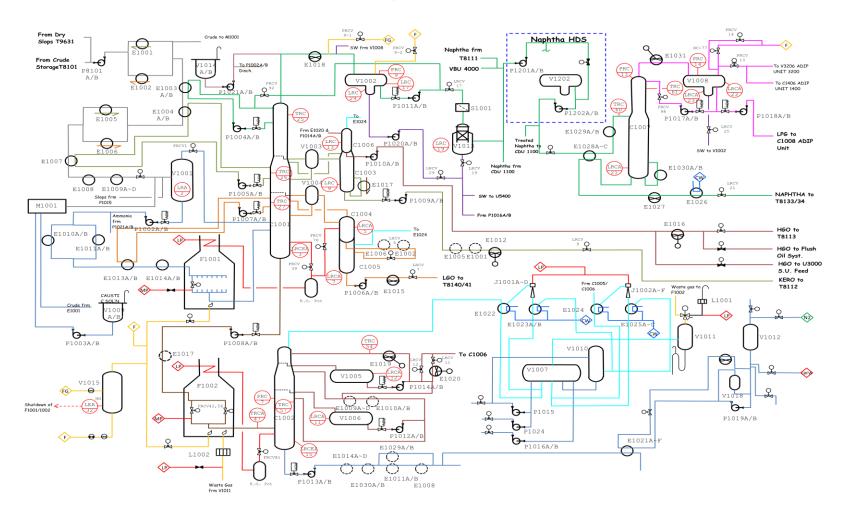
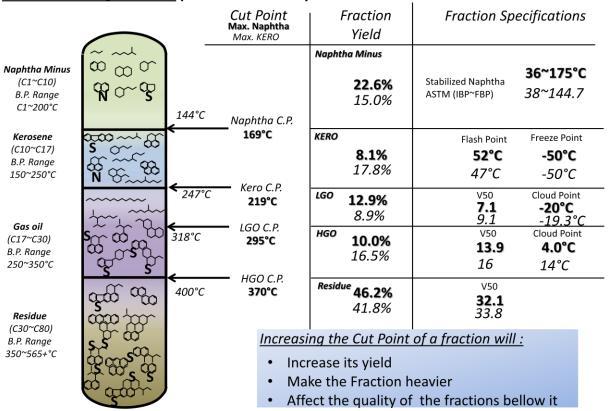
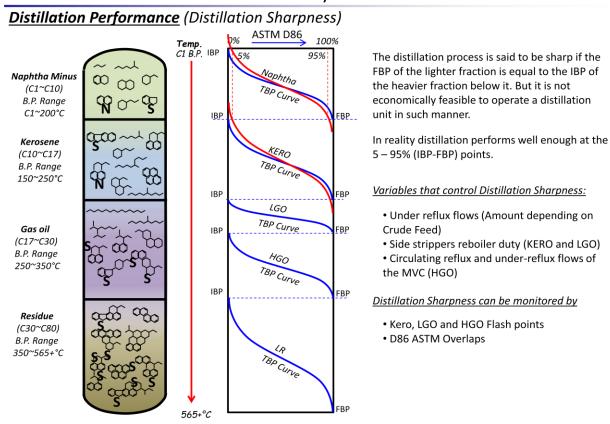
CDU Simplified Scheme



Distillation Performance (Cut Point & Yield)



Main Refinery Processes



Distillation is said to be sharp if the IBP of the lighter fraction is equal to FBP of the heavier fraction.

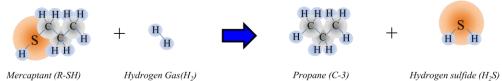
Hydrotreating

Reaction Basics

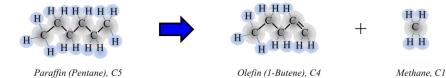
What is a Chemical Reaction?

It is a process of changing the form of a chemical into another chemical of a different identity. It can be done ...

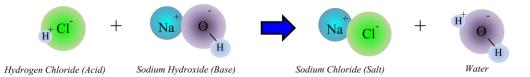
☐ By combining with other chemicals- Example: Hydrogenation of organic sulfur compounds



☐ By breaking into other chemicals - Example : Thermal Cracking of Paraffins

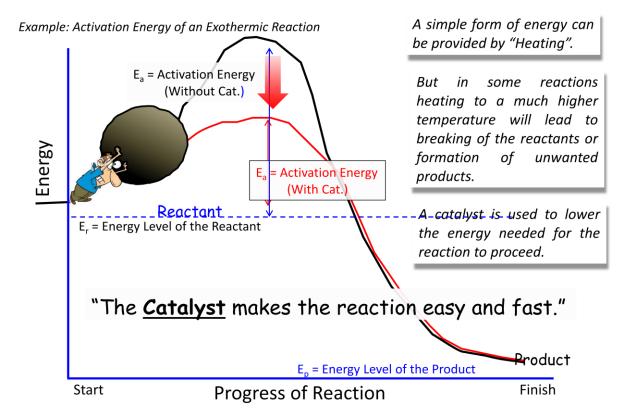


☐ By exchanging elements - Example : Neutralization (Acid/Base Reaction)

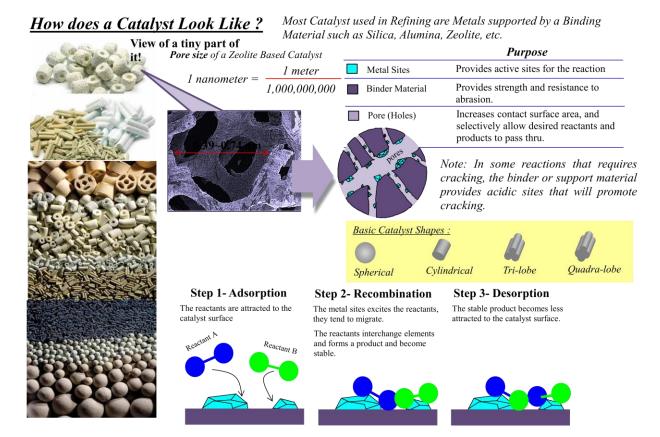


Reaction Basics

"Some reactions need certain amount of Energy to proceed."



Reaction Basics



Refinery Configuration

Important Hydroprocessing Reactions

1. Hydrotreating

2. Aromatics Saturation

$$+ 2H_2 \rightleftharpoons \bigcirc + 3H_2 \rightleftharpoons \bigcirc$$

3. Hydrocracking

4. Isomerization

What is Hydrotreating?

It is a moderate	to high	tempe	erature &	pre	essure	catal	ytic rea	action	betwe	en
hydrocarbon &	hydroger	n gas	intended	to	remov	e or	reduce	organ	ic Sulf	fur,
Oxygen and Nitro	ogen.									

☐ Unsaturated hydrocarbons (Olefins & Aromatics) are also stabilized in hydro treating by replacing the weak & unstable double/triple bond sites with hydrogen.

What is the purpose of Hydrotreating?

- 1. In Naphtha High Nitrogen and Sulfur content (> 1ppm) will poison Platformer Catalyst
- 2. In KERO Jet Sulfur specification max. 0.2% wt.
- 3. In Gas Oil Sulfur is removed to comply with government regulations for AGO (500~10 ppm)
 - Saturation of olefins and aromatics will improve CETANE of AGO

"But Saturation of olefins and aromatics is a reversible reaction, high concentration of hydrogen must be kept to prevent backward reaction."

Main Refinery Processes

Environmental Legislation Trends

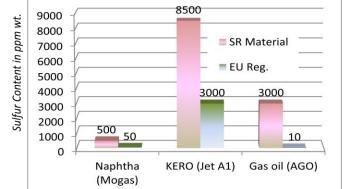
Main Drivers & Players for the Demand on Cleaner Fuels

- ☐ Environmental and Health Concerns
- Air quality: Particulates, Hydrocarbons, NOx, Smog
- > CO2 Emission (Kyoto Protocol)
- Acid Rain (SOx)

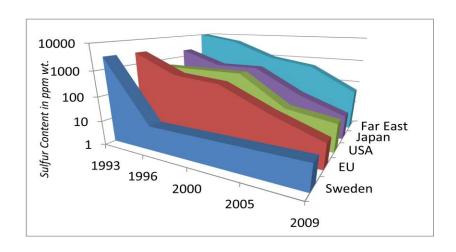


- ☐ Government, Car Manufacturers (Worldwide Fuels Charter), Oil Industry, Customers – complex discussions.
- ☐ Exhaust treatment systems require low Sulfur Fuels: Longer life time and higher efficiency.



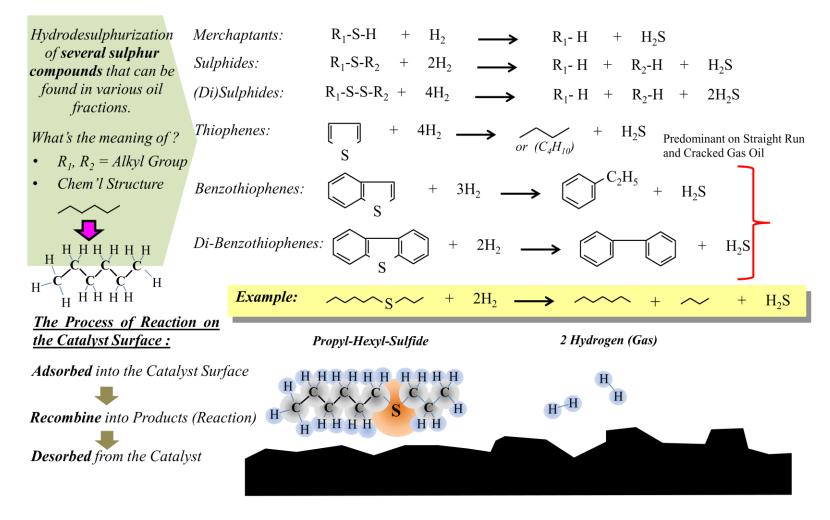


Development of AGO Specs 1993~2009 by Geographical Area (ppmwt Sulfur – Logarithmic)

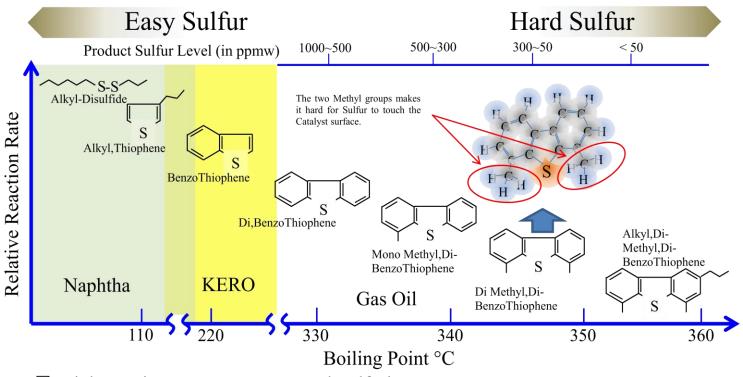


Reactions that happens in Hydrotreating:

1. Hydrodesulphurization – removal of sulfur by breaking Carbon to Sulfur (C-S)Bonds and replacing it with C-H and H-S bonds.



Hydrodesulphurization Reaction Rate of Different Organic Sulfur Compounds vs. Boiling Point



- ☐ High reaction rate means easy to desulfurize.
- ☐ More complex molecules are more difficult to desulfurize.
- ☐ Lighter materials are easier to desulfurize than heavy materials.
- ☐ A lower sulfur content requirement of Gas Oil needs desulfurization of the more complex sulfur compounds.

Sulfur Compounds in Decreasing Reactivity Order: Mercaptants > Disulfides > Sulfides > Thiophenes > Benzothiophenes > Alkylbenzothiophenes

Reactions that happens in Hydrotreating:

2. Hydrodenitrogenation – removal of nitrogen by breaking Carbon to Nitrogen (C-N)Bonds, needs more Hydrogen (Higher partial Pressure) and higher Reaction temperature compared to Hydrodesulphurization.

Hydrogenolysis of Some Nitrogen Compounds

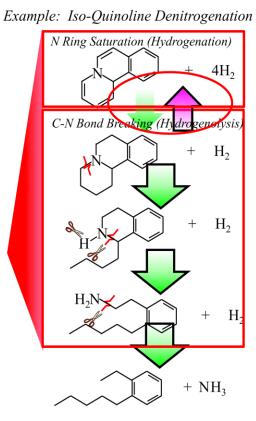
Aniline
$$\longrightarrow$$
 + H_2 \longrightarrow + NH_3

Pyridine \longrightarrow + $3H_2$ \longrightarrow + $2H_2$ \longrightarrow C_5H_{12} + NH_3

Quinoline \longrightarrow + $2H_2$ \longrightarrow

Some Facts About Hydrodenitrogenation:

- The concentration of Nitrogen compounds in straight run fractions is very small compared to cracked oils (TGU/VBU).
- Denitrogenation require Hydrogenation of the ring containing Nitrogen before hydrogenolysis of C-N Bond proceeds.
- Hydrogenation reaction is reversible and to favor a forward reaction hydrogen concentration must be kept high.
- *C-N double bond is stronger than C-N single bond.*
- *C-N bond breaking requires large energy compared to C-S bond breaking.*



What is meant by "Equilibrium Reactions"?

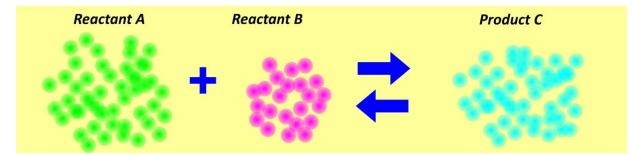
Equilibrium reactions or reversible reactions are reactions where products are formed back into reactants at certain product concentration or condition that allows a backward reaction to happen.

Example: Consider Reactant "A" and Reactant "B" undergoes reaction to form Product "C"

□ "A" and "B" will be consumed as "C" is being formed
□ In a reversible reaction "C" can also form "A" and "B"
□ At certain concentration of "A", "B" and "C" in the system equilibrium is achieved
➤ "You would think the reaction stopped"
➤ "Actually No" Its just that; the speed of "A" & "B" forming to "C" is equal to "C" forming back to "A" & "B"
□ Without intervention we end up with incomplete conversion of A & B or less C produced.
□ Solution: Remove C from the system continuously so that a net forward reaction is possible.

How to remove "C" from the System?

- ☐ If the reaction happens with "A", "B" and "C" are in Gas form; "C" is condensed to liquid. (SRU)
- ☐ Or convert "C" to "D" (Another Product) like in HDN.



Main Refinery Processes

Reactions that happens in Hydrotreating:

3. Hydrodeoxygenation – removal of oxygen from oxygen compounds (Oxygenates) by breaking Carbon to Oxygen (C-O) bonds.

Hydrogenolysis of Some Oxygenates:

Phenols H_2 H_2 H_3 H_4 H_4 H_5 H_5 H_4 H_5 H_5 H_5 H_5 H_5 H_5 H_6 H_7 H_7

4. Hydrogenation of Aromatics and Poly-Aromatics – Saturates the double bonds present in the aromatic structure forming Naphthenic compounds.

Hydrogenation of Naphthalenes:

Other Reactions that happens in Hydrotreating:

At 300~500°C & Hydrogen Partial Press. Up to 300 Bar abs.

- Increase of temperature and decrease of hydrogen partial pressure favors the backward reaction.
- ☐ Increase of Condensed Ring Concentration and Number of Alkyl chains per Polyaromatic molecule will make the reaction difficult.
- 5. Hydrocracking Under high temperatures (360~400°C) and high Hydrogen Partial Pressures, large molecules are broken down to smaller molecule by a C-C Bond breaking. Under HDT conditions and proper catalyst selection this reaction can be avoided.
- 6. Aromatics Condensation Under low hydrogen partial pressure and high temp. ring formation is favored and these complex ring structures are built up as "Coke", coke has a coating effect on the catalyst active sites, thus cause catalyst deactivation.

Main Refinery Processes

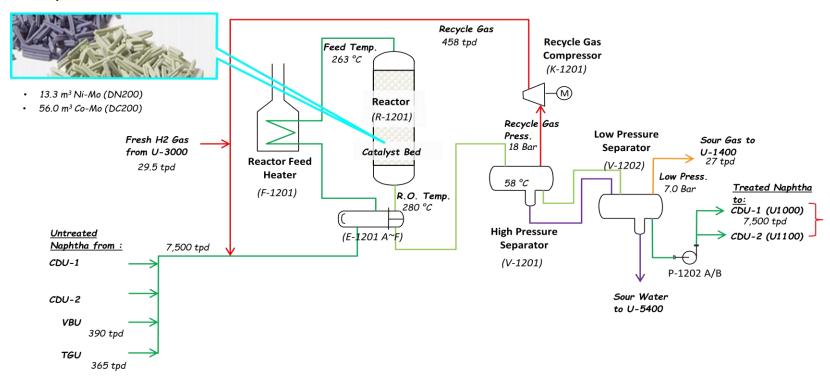
Summary of Hydro Treating Units:

Unit	Feed	Purpose	Reaction Condition	Heat Gen.
U-1200 Naphtha HDS	Naphtha produced from CDU's, VBU & TGU	Reduce Sulfur in naphtha.	Vapor phase @ 320~380°C, and abt. 32Barg Outlet Press. Hydrogen is recycled to increase H2 Partial Pressure and reduce the risk of coke formation.	
U-1300 KERO HDS	Kerosene produced from CDU's	 Reduce Sulfur in Kerosene. Improve stability of Kerosene by olefin saturation 	Trickle phase @ 355°C, and abt. 40 Barg Outlet Press. Hydrogen is recycled to increase H2 Partial Pressure and reduce the risk of coke formation.	
U-1400 Gasoil HDS	GasOil produced from CDU's, VBU & TGU	 Reduce Sulfur in Gasoil. Improve stability. Improve Cetane 	Trickle phase @ 360°C, and abt. 50 Barg Outlet Press. Hydrogen is recycled to increase H2 Partial Pressure and reduce the risk of coke formation.	
U-7100 Platformer Hydro Treater	Naphtha produced from CDU's or HCU	Removal of metallic compounds (Permanent Poisoning of Platformer Catalyst) Removal of Sulfur/Nitrogen (Temporary Poison)	abt. 13 Barg Outlet Press. Hydrogen is recycled to increase H2 Partial Pressure and reduce the risk of coke formation.	

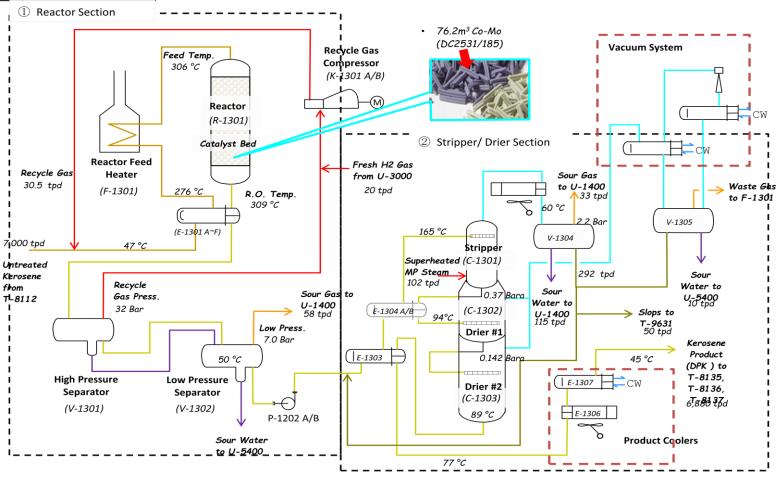
Other reactions:

- Nitrogen in Naphtha is also removed by forming Ammonia (NH₃).
- Oxygen in Naphtha is also removed by forming Water (H₂O)
- Unsaturated Hydrocarbons (Olefins) are saturated improving product stability.

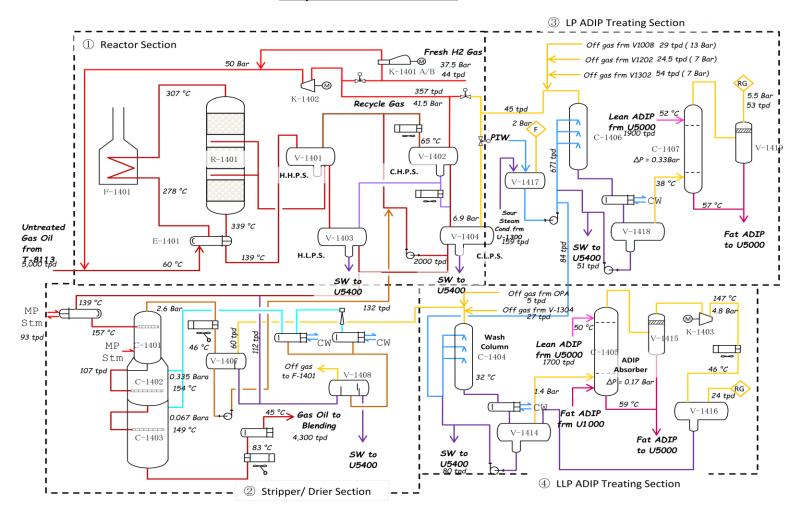
Simplified Process Flow:



Simplified Process Flow:



Simplified Process Flow:



Thermal Conversion "Is the conversion of large molecules into smaller ones ("Cracking") by application of high Temperature." Hydrocarbons with large molecules when heated to temperature above 400°C breaks into hydrocarbons of smaller molecules. A spontaneous, non selective disintegration of hydrocarbons producing molecules of all molecular weights and boiling points Causes redistribution of hydrogen forming lighter products having more hydrogen than the feed and heavier products having lesser hydrogen than the feed.

"Important practical result of cracking is the reduction of viscosity of the product caused by the presence of smaller molecules."

Thermal Cracking is commonly used in oil refineries for the following purpose:

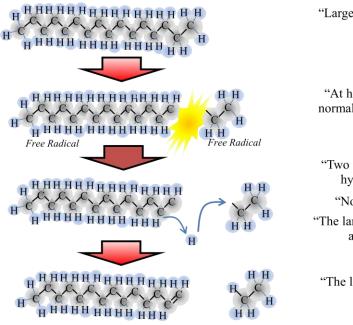
- 1. Thermal Cracking for viscosity reduction (Visbreaking)
- 2. Manufacture of Thermal Gas Oil
- 3. Manufacture of briquetting Bitumen
- 4. Manufacture of Carbon Black Feedstock
- 5. Coking

Survey of Currently Applied Thermal Cracking Processes

Process & Operating Conditions	Feed	Purpose	Yield on Feed	
Visbreaking • 430~490°C	•Long Residue	•Viscosity Reduction	•10~30% m N0.2 Fuel gain	
•2~10 min res. Time •2~20 Bar •No recycle	•Short residue			
Thermal Gas Oil				
• 470~490°C •1~4 min res. Time •2~25 Bar •CFR 1~2	•Long Residue •Flashed Distillate	•Gas oil Production (165~350°C)	•20~40% m Gas Oil	
Coking (Not in SASRE	EF)			
• 480~500°C •Hrs of res. Time •3~10 Bar •CFR 1~1.3	•Long Residue •Short Residue	•Coke or Cat. Cracker feed	•5~30% m coke •50~60% m Cat Cracker feed	
Thermal Cracking for Ga	asoline (Not in SASF	REF)		
• 480~500°C •20 Bar •CFR 2~3	Long ResidueShort ResidueCat. CrackedCycle oil	•Gasoline Production with MON 60~70, RON 68~78	•10~30% m Gasoline	

Decomposition of Different Types of Hydrocarbon

1. Paraffins - Undergo mostly decomposition and dehydrogenation reactions



"Larger molecules decompose easily than smaller molecules"

"At high temperature C-C bond breaks, normally 1~3 carbons from the extremes"

"Two molecules are formed needing two hydrogen atoms (Free Radicals)"

"No Hydrogen gas is added, so ..."

"The larger molecule donates one hydrogen atom to the smaller molecule"

"The larger molecule forms a C=C bond, become olefinic"

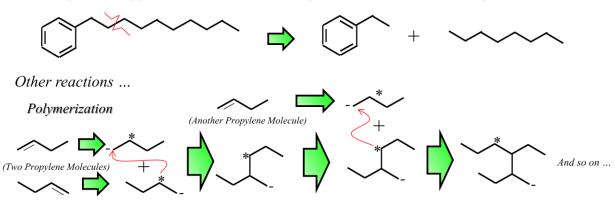
Smaller molecules with higher hydrogen content than the feed and Larger molecules with lower hydrogen content is formed.

Decomposition of Different Types of Hydrocarbon Cont'd ...

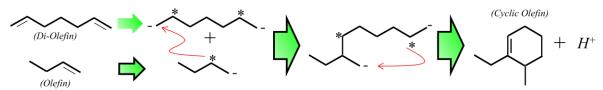
2. Olefins - Undergo the same decomposition and dehydrogenation reactions as paraffins.

3. Naphthenes and Aromatics

- The aromatic and naphthenic ring structure is very stable and will not decompose easily.
- Decomposition happens on the side chains leaving 1~2 carbon chains on the ring structure.

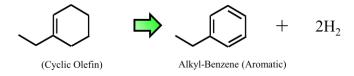


Cyclic Olefin Formation of Olefin and Di-olefin



Other reactions continued...

Dehydrogenation of Cyclic Olefins & Naphthenes



Condensation of Aromatic Sustituents

$$\begin{array}{c} \\ \\ \\ \\ \\ \end{array}$$

Products of Thermal Reaction

☐ Gas

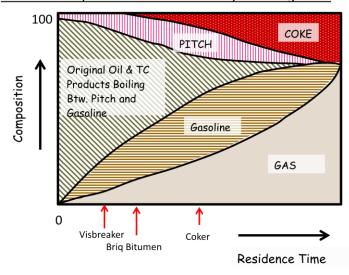
☐ Gasoline (Naphtha)

☐ Products Boiling above Naphtha but below Feed Boiling Range.

☐ Converted and unconverted products in the feed boiling range.

☐ Products boiling above feed boiling range including coke

Product Composition as a Function of Cracking Time



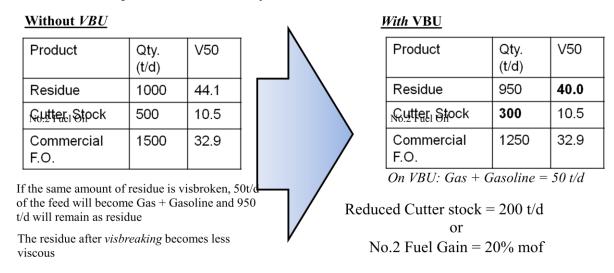
At zero time the composition is that of the feed; gas or light distillates produced as the reaction proceeds has higher hydrogen content than the feed this is accompanied by production of heavy products containing less hydrogen, further into the reaction intermediate products disappear leaving gas (Highest Hydrogen Content) and coke (Lowest Hydrogen Content)

Visbreaking

Is operated for the primary purpose of reducing viscosity by breaking some high molecular weight fractions of the residue into smaller molecules.

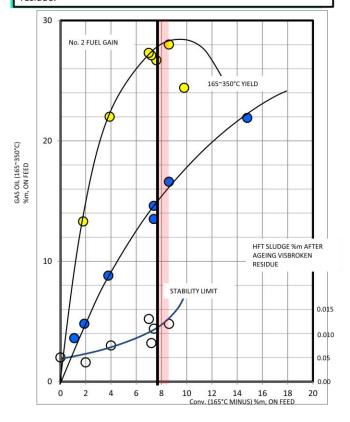
Normal Feedstock: Short Residue from HVU Alternative Feedstock: Long Residue from CDU

The viscosity reduction leads to a lower cutter stock requirement for F.O. Blending, a better middle distillate position in the refinery as a whole.



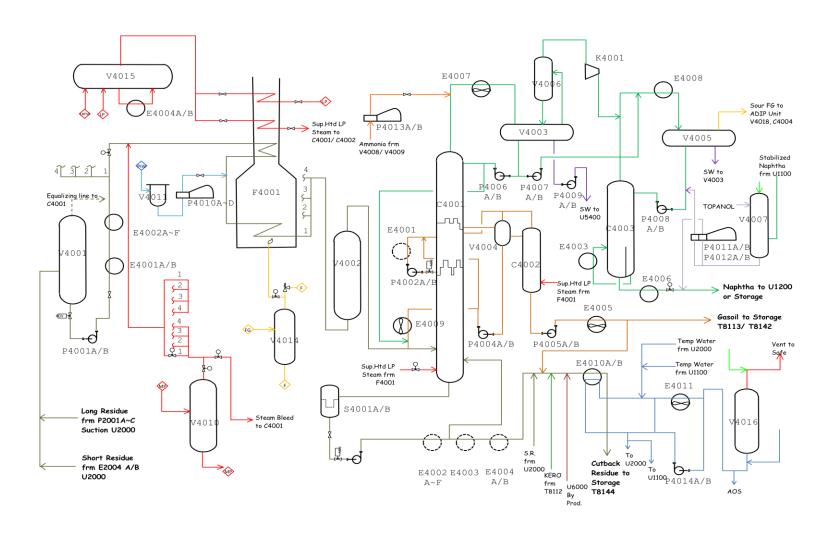
The basic aim of visbreaking is to maximize No.2 Fuel gain.

But Cracking severity is limited by the sludge content of the TC residue.



Typical Set of Visbreaking Data

Feed Type	Unit	Short Residue
Feed Properties		
D 15/4		1.010
V50		42.0
Hydrogen	%m	10.4
Gas Oil in Feed	%mof	0
Yield on Crude	%moc	28.8
Yields	%mof	
Gas (C1~C4)		1.9
Gasoline (C5~165°C)		4.1
Gas Oil (165~350°C)		11.7
350°C+ residue		82.3
Properties of Products		
V50 of 165~350°C Gas Oil		9.3
V50 of 350°C+ residue		40.5
V50 of 165°C+ residue		36.6
ΔV50 of Process		5.4
No.2 Fuel Gain	%mof	25.1
Visbreaking Selectivity		4.2
Thermal Gas Oil Yield	%mof	11.7
Gas oil produced by cracking	ng %mof	11.7
Gas Oil Selectivity		2.0
Net Fuel Consumed	%mof	1.2



Hydrocracking

Removes heteroatoms (Sulfur, Nitrogen, Oxygen compounds), saturates aromatics olefins thru hydrogenation that in turn results large molecules to crack into smaller molecules.

The objective of hydrocracking is to reduce the boiling point of the feedstock by increasing the hydrogen content and hence reducing the average carbon number per molecule.

It is a catalytic reaction at high temperature and pressure under hydrogen-rich atmosphere.

Catalyst - Hydrocracking catalyst is bifunctional, two types of catalytic chemistry is carried out to achieve the desired reaction

Two Functions of the Catalyst

- 1. **Metallic or Metal-sulfides (NiMo, NiTu)** promotes hydrogenation, hydrotreating, aromatic and olefin saturation reactions
- **2. Acidic Site (Alumina)** promotes cracking of hydrocarbons; it also serves as a binding material of the catalyst.

Hydrocracking Chemistry

Hydrocracking process feeds are complex mixtures of paraffinic, alkylated (poly)-aromatic and naphthenic molecules, it also contains Hetero-Atoms, mainly sulfur, nitrogen, oxygen and a lesser number of metals (Ni and V).

Reactions that can be found in Hydrocracking:

- 1. Hetero-atom Removal
- 2. Hydrogenation
- 3. Ring-Opening
- 4. Hydrodealkylation
- 5. Cracking
- 6. Isomerization
- 7. Condensation



1. Hetero-atom Removal Reactions

(HDN, HDS, HDO)

HDN – Hydro denitrogenation reaction is very important since it has the effect of neutralizing the acid site of the catalyst hence affecting cracking reaction.



(Normally 500~2000 ppmw of Feedstock)

HDS – Hydro desulfurization reaction is easily proceeds under normal hydrocracking conditions.

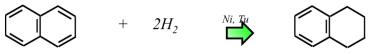


HDO- Hydro deoxygenation reaction is easily proceeds under normal hydrocracking conditions.



(1.0.man) coo zooopp.... oj recusio

2. Hydrogenation Reaction - Is mainly saturation of Aromatics and Olefins

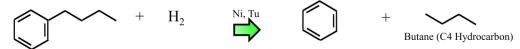


- 3. Hydro-decyclization or Ring Opening Reaction
 - Is ring opening of naphthenic rings, usually follows Aromatics Saturation since aromatics ring opening does not happen directly.



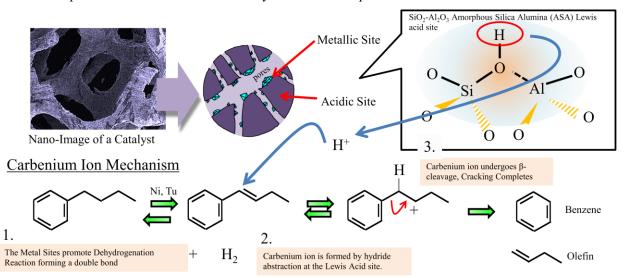
4. Hydrodealkyllation (HDA) Reaction

- Unlike thermal cracking, hydrodealkyllation completely cracks the alkyl group attached to the aromatic structure

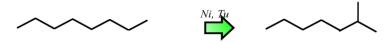


5. Hydrocracking Reaction

Takes place at the Acidic site of the catalyst and can be explained thru the carbenium ion mechanism.



6. Isomerization Straight chain hydrocarbons (Paraffins) becomes branched (Isoparaffins)



7. Condensation Aromatics with oxygen substituents reacts with each other to form a larger polyaromatic structure called Poly-cyclic aromatics (PCA) or Poly-nuclear Aromatics (PNA) which are potential coke precursors.

Coke is partly responsible for catalyst activity loss and can cause fouling of equipment in the reactor effluent train.

Hydrocracking Reactions according to decreasing speed.

HDO > HDS > HDN > Aromatic Saturation > Hydrodealkyllation of Aromatics > Naphthene Conversion > Paraffin Conversion

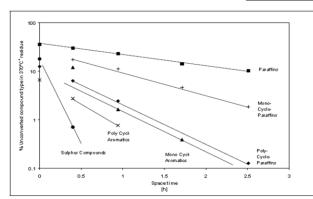


Figure 2.1 Hydrocracking of Kuwait Vacuum Gas Oil - % unconverted 370°C* residue as a function of space time for various compound types (after Ref. 2, 10)

Hydrocracking

A plot of the Reactor Effluent % Unconverted Components vs. Space-time (Reaction Time)

The speed of reaction can be seen by observing the slopes of the line; Sulfur Compunds has the stiffest slope and therefore the fastest of the reactions, while Paraffins is the slowest.

Exothermic Reaction

The reactions occurring in hydrocracking are highly exothermic due to the consumption of Hydrogen, as opposed to dehydrogenation reactions such as (Reforming, Cat, Cracking)

Because of its exothermic nature, the catalyst in the fixed bed reactors are distributed with a limited volume, and a cold quench gas is applied after each bed.

Reaction Temperature

Since the temperature across the reactor is increasing it is difficult to directly identify the reaction temp.

<u>Weighted Average Bed Temp (WABT)</u> is defined to represent the reaction temperature across the reactor.

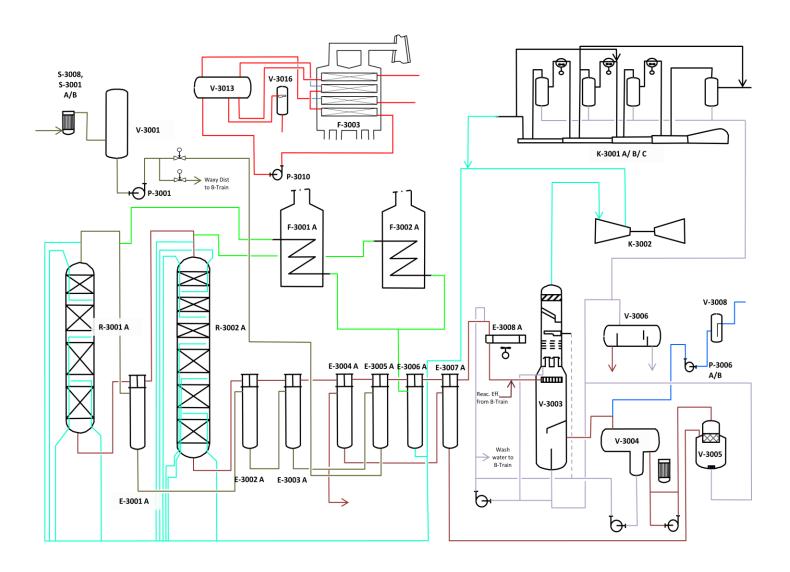
For a k number of beds, each with a weigh fraction, x_i of the total catalyst weight in the reactor.

WABT =
$$\sum_{j=1}^{k} X_j \cdot \left[(1-a) \cdot T_{\text{in},j} + a \cdot T_{\text{out},j} \right]$$

Values for the constant a vary between 0.667 in the first stage to 0.4 on the second stage due to the different temperature profiles over the beds.

Hydrocracking Products

	Relevant Quality	Comments		
Gas/LPG (C1~C4)	Iso-/normal butane ratio = $1.5\sim3$	Higher than S.R. Material		
Mogas –Tops (C5~82°C)	Iso/ Normal C5,C7 ratio = 2~7	Higher than S.R Material		
	RON =76~86, MON = RON+1			
Mogas- Naphtha (82~180°C)	Sulfur = 0.5~50 ppmw	Depending on crude origin		
	P/N/A range from 40/45/15 ~ 55/40/5 %wt	Towards EOR, A increases N decreases		
Kerosene (180~250°C)	Smoke Pt. = 11~33 mm	Depending on crude origin		
	Sulfur < 50 ppmw	Bad for lubricity		
	Freezing Pt = -44°C	Synergistic effect when blended with S.R. Kero		
Gasoil (250~370°C)	Cetane Index = 40~65	Depending on Crude and operating conditions		
	Cloud Pt.= -25~10°C	Depending on crude origin		
Hydrowax (370°C plus)	BMCI = 10~25	Depends on Crude, Reaction and Fractionation Cond'n		



Catalytic Reforming converts naphtha with boiling point range of 80~185°C into an aromatic rich, high octane reformate product, with hydrogen as the main by product.

Naphtha feed to Platformer typically C6~C12 Parrafins, Naphthenes and Aromatics

A naphtha with higher naphthenes and low on paraffins is a good platformer feed.

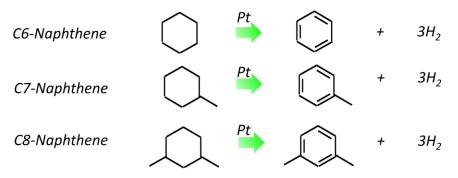
Straight Run Naphtha – more paraffinic, bad platformer feed.

Naphtha from Thermal Cracking and Hydrocracking – more naphthenic, good platformer feed.

Reactions involved in Platforming

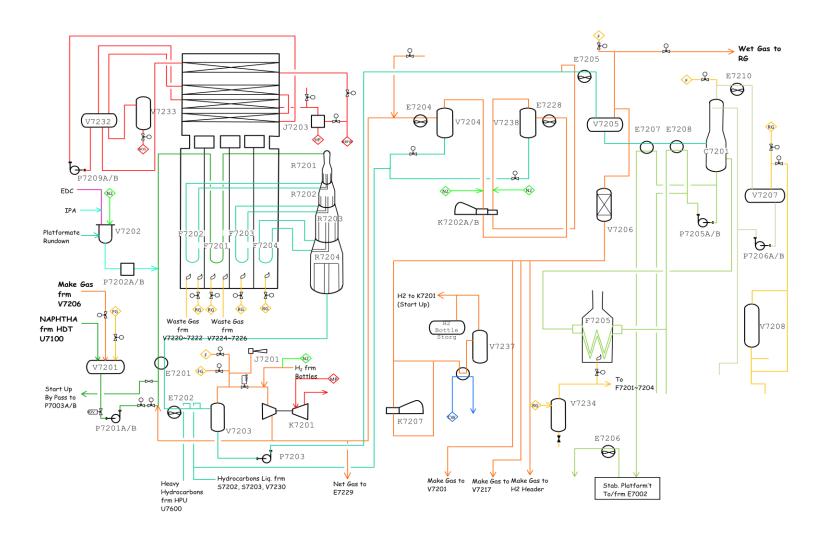
Dehydrogenation of Naphthenes

The reaction is extremely rapid and is favored by high reactor temperatures and low pressure

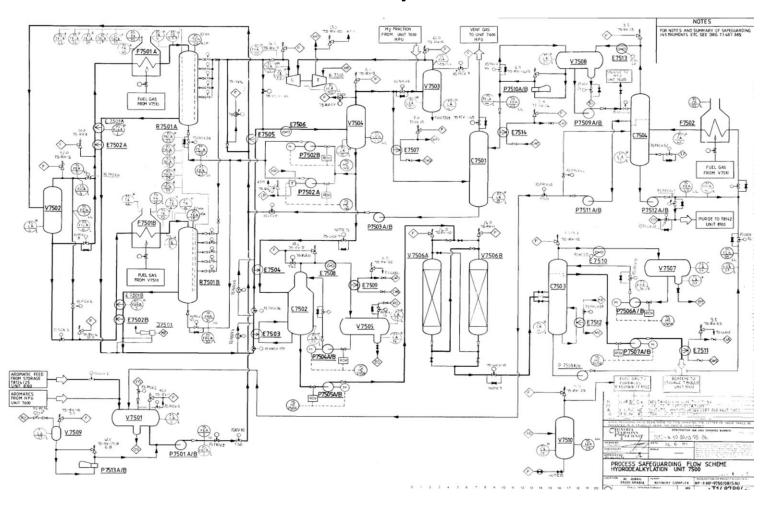


Indications of High Dehydrogenation Reaction

- ☐ Large temperature drop across Reactor 1
- ☐ High Hydrogen Production
- ☐ High Hydrogen Purity



Main Refinery Processes



Main Refinery Processes

