



Republic of Iraq
Ministry of Higher Education
and Scientific Research
Al-Mustaqbal University College
Chemical Engineering and Petroleum Industries
Department

Subject: Oil and Gas Field Processing
3rd Class

Lecture 7 Part 2

Cracking

Cracking means heating of higher boiling petroleum fractions like heavy fuel oil at high temperature and pressure to produce lower boiling lighter fractions. It is an endothermic reaction.

The process of cracking, increases the relative amounts of the lower hydrocarbons. During cracking, carbon-carbon bonds get broken, leading to various kinds of products being formed.

There are two types of cracking:

- 1- Thermal Cracking:** Cracking at elevated temperatures in the absence of catalyst. Examples: Visbreaking, delayed coking, Fluid coking.
- 2- Catalytic Cracking:** Cracking in presence of catalyst. Examples: FCC , Hydrocracking, DCC.

1- Thermal cracking

Breaking down large molecules by heating at high temperature and pressure is termed as thermal cracking.

There are three classes of industrial thermal cracking processes:

a- Visbreaking

The first is mild cracking (as in visbreaking) in which mild heating is applied to crack the residue just enough to lower its viscosity and also to produce some light products.

Feed : Atmospheric residue (AR) & Vacuum residue (VR)

Products : Four products are produced in the visbreaking process: gases (C₄), Naphtha C₅ - 166 °C (C₅ -330 F), gas oil 166–350 °C (330–660 F) and residue or tar 350+ °C (660+ F).

b- Delayed Coking

The second process is delayed coking in which thermal cracking converts the residue into lighter products, leaving coke behind.

Feed: Vacuum residue, cracked residue.

Product: Gases, Naphtha, Fuel oil, Gas oil and Coke.

A schematic flow diagram of the delayed coking is shown in Figure below. The process includes a furnace, two coke drums, fractionator. Residual oil from the vacuum distillation unit is pumped into the bottom of the distillation column called the main fractionator. From there, it is pumped, along with some injected steam, into the furnace and heated to its thermal cracking temperature of about 480 °C. The injected steam helps to minimize the deposition of coke within the furnace tubes. The liquid–vapour mixture leaving the furnace passes to one of the coking drum, and cracking takes place in the drum. Coke is deposited in this drum for 24 h period. After the first drum is full of the solidified coke, the hot mixture from the furnace is switched to the second drum. While the second drum is filling, the filled first drum is steamed out to reduce the hydrocarbon content of the petroleum coke, and then quenched with water to cool it. Vapors from the top of the coke drum are returned to the bottom of the fractionator. These vapors consist of steam and the products of the thermal cracking reaction (gas, naphtha and gas oils). The top and bottom heads of the full coke drum are removed, and the solid petroleum coke is then cut from the coke drum with a high pressure water nozzle, where it falls into a pit, pad, or sluiceway for reclamation to storage.

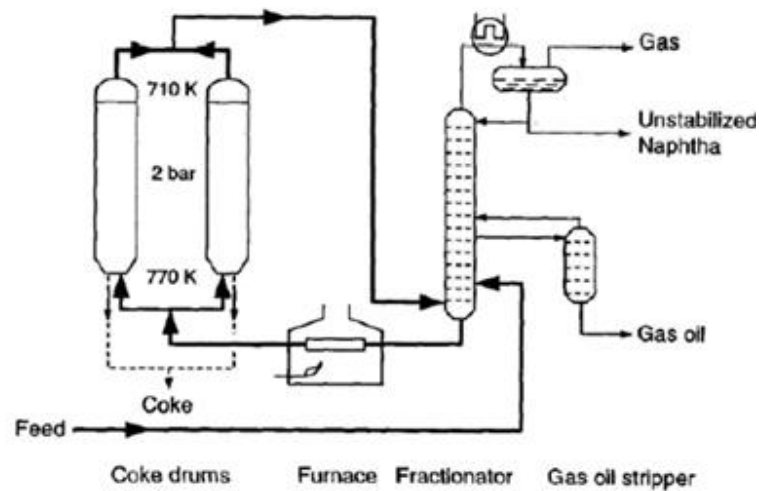


Figure : Process Flow Chart of Delayed Coking

c- Fluid Coking and Flexi Coking

The third process involves severe thermal cracking. Flexi coking is one of the most important processes in a refinery as only 2% of coke is produced from the residue. It is continuous process involves thermal cracking in a bed fluidized coke and gasification of the coke produced at 870 °C.

2- Catalytic Cracking:

Higher hydrocarbons can also be cracked at lower temperature (350-650 °C) and lower pressure (2 atm) in the presence of a suitable catalyst. The feedstocks ranging from gas oil to heavy crude oil and residuum is heated in presence of catalyst (like, platinum , nickel , iron silica-alumina etc..) to produce lower boiling products and gasoline of higher octane number and therefore this method is used for obtaining better quality gasoline. Modern cracking uses zeolites as the catalyst.

Advantages of Catalytic Cracking over Thermal Cracking:

- Pressure and temperature required for catalytic cracking is lower.
- Yield and octane number of petrol production is higher.
- Petrol produced has less quantity of gum and gum forming material.
- Sulphur content of the products is low.
- The product contains a higher amount of aromatics and hence the petrol possesses better anti-knock characteristics.

Reforming

Reforming means rearrangement of molecules without much affecting the average molecular weight of feed which is generally naphtha and heavy gasoline. Reforming is carried out to produce high quality (octane number) gasoline by heating with or without catalyst.

Feed for Reforming:

The feed is generally naphtha produced during straight run distillation of crude oil, catalytic cracking and cooking process. The best result is obtained with naphtha **produced during straight run distillation** having high naphtha content.

Reforming Product:

Besides the main product (reformate) or reformat gasoline, reforming also produces lighter hydrocarbons (gases), hydrogen and traces of very high boiling materials.

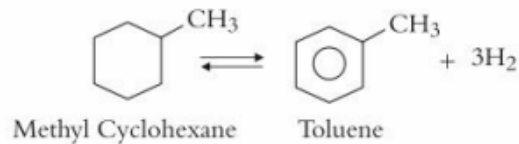
Reforming Reactions :

There are four major types of reactions that occur during reforming processes:

1. Dehydrogenation

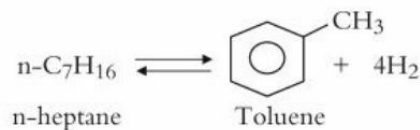
Dehydrogenation is the process by which hydrogen is removed from an organic compound to form a new chemical.

Dehydrogenation of naphthenes to aromatics and hydrogen.



2. Dehydrocyclization

dehydrocyclization of paraffins to aromatics and hydrogen.



All the above reactions are highly endothermic.

3. Isomerization

Isomerization is the process in which light straight chain paraffins of low octane number are transformed into branched chains with the same carbon number and high octane numbers.

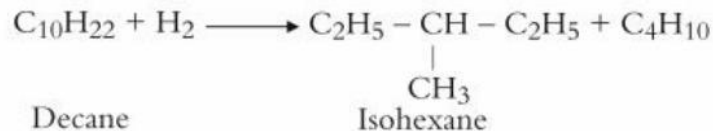


Isomerization is a mildly exothermic reaction and leads to the increase of an octane number.

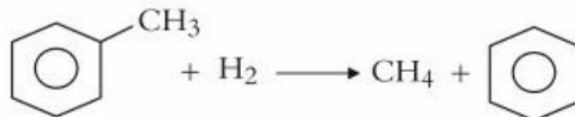
4. Hydrocracking

Hydrocracking reactions are the main sources of C₄ hydrocarbons (C₁, C₂, C₃ and C₄). The reactions are highly exothermic and consume high amounts of hydrogen. Cracking results in the loss of the reformate yield.

Paraffin hydrocracking:



Hydrocracking of aromatics



Other paraffins can crack to give C₁-C₄ products.

Types of Reforming:

Reforming can be thermal or catalytic as in the case of cracking. Catalyst apart from accelerating the process also enhances the yield and quality (octane number) of gasoline. The gasoline produced by reforming is called reformed gasoline or reformate. Thermal reforming has been almost completely replaced by catalytic reforming.

- Thermal Reforming

This is carried out in absence of catalyst and its similar to high temperature, low pressure thermal cracking. Feed is usually Naphtha and the products are mainly gas (13 -14%) and gasoline (75 -80%) of octane number 81 -86, rest being polymer (unwanted gum) and losses.

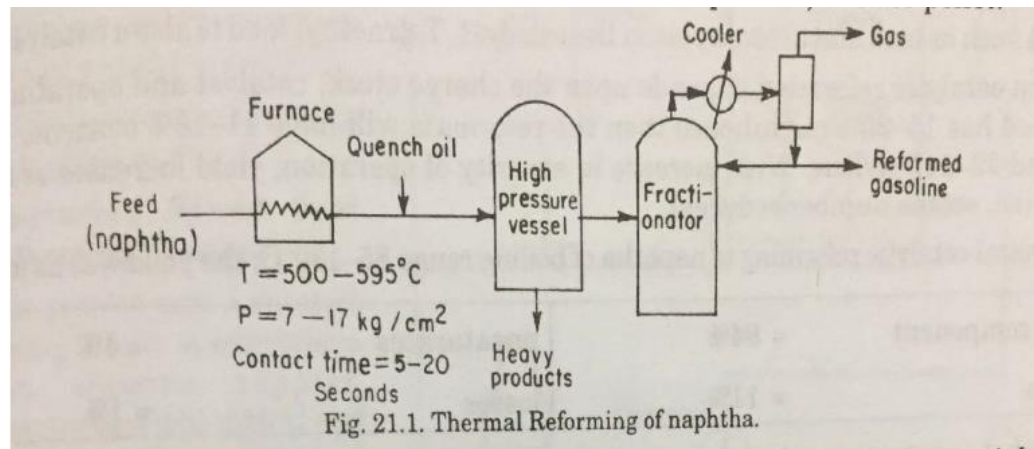


Figure: Thermal Reforming of Naphtha

- Catalytic Reforming

Reforming in the presence of a catalyst is called catalytic reforming.

There are two types of catalyst are used:

- Non- precious metal oxide type (e.g. molybdena or chromia supported on alumina base).
- Precious metal oxide type (e.g. platinum on a silica-alumina or alumina base).

Platinum is more active and selective catalyst.