Lecture №7

Cracking of Straight Run Residue

The processing, in which certain components of petroleum fractions undergo chemical changes.

The fractions obtained during the primary distillation are almost never ready-made commercial products, because their quality does not meet the various requirements:

- •Direct gasoline has an ON of no more than 60;
- •Kerosene and diesel fuel contain large amounts of sulfur;

•Diesel fuel also contains linear paraffins.

Since during the primary distillation of oil, an increase in the production of gasoline leads to the accumulation of heavy fractions, arose the need to convert these fractions into lighter fractions.

Main catalytic processes	Thermal (destructive) processes	Processes with hydrogen (catalytic)
Catalytic cracking	Thermal cracking of liquid petroleum feedstock under high pressure (20 - 70 atm)	Hydrotreating
Reforming	Thermal cracking of oil residues at low pressure (coking, destructive distillation)	Hydrocracking
	Pyrolysis of liquid and gaseous petroleum raw materials	Hydroiso-merization

Cracking

Cracking - high-temperature processing of oil and its fractions in order to obtain, as a rule, products of lower molecular weight - motor fuel, lubricating oils, etc., as well as raw materials for the chemical and petrochemical industries. Cracking occurs with the rupture of C-C bonds and the formation of free radicals or carbanions. Simultaneously with the breakdown of the C-C bonds, dehydrogenation, isomerization, polymerization and condensation of both the intermediate and the starting materials take place. As a result of the last two processes, so-called-cracking residue (fraction with a boiling point of more than $350 \circ C$) and petroleum coke are formed.



Thermal vs. Catalytic

Particulars	Thermal Cracking	Catalytic Cracking
Definition	Breaking of Larger Hydrocarbons into smaller ones by the application of Heat Alone is known as Thermal Cracking	Breaking of Larger Hydrocarbons into smaller ones by the application of Heat in presence of catalysts is known as Catalytic Cracking
Temperature	400 – 1000 °C	Reactor Temperature: 470 – 540 °C Regenerator Temp: 591 – 610 °C
Regenerator	Not Required	Required for catalyst recovery
Waste Generation	Large amount of coke is generated	Coke formation is low
Pressure	10 - 15 kg/cm ²	< 5 kg/cm ²
Mechanism	Free Radical Mechanism	Carbonium Ion Mechanism
Pre-treatment of feed	General treatments are sufficient, eliminating non volatile gases and removal of S and N.	Highly specific and immense to safeguard the life of catalyst, along with S removal.
Products	Generally, ring structures and unsaturates	Generally, focused on producing gasoline of high octane value

Thermal cracking

The process of thermal cracking of heavy oil residues in the world oil refining practically lost its "gasoline-producing" meaning. At present, this process is a thermal preparation of distillate raw materials for coking plants and production.

<u>Thermal gasoil</u> - raw material for the subsequent production of carbon black (soot).

Methods of conducting the process:

a) in the liquid phase at a temperature of 500-540°C and a pressure of 2-7 MPa (more gasoline is formed);

b) in the vapor phase at a temperature of $550-600^{\circ}$ C and a pressure of 0.2-0.5 MPa (more gaseous is formed).

The thermal cracking of the straight run residue was for many years the most important process supplementing the straight run gasoline, and many such units were built in various countries.

However, many such units still exist in less developed countries, for instance in Eastern Europe, and their conversion and improvement is an important problem for these countries. *Feedstock:* vacuum distillation residue, sometimes heavy gasoil and gasoil recycle stock from cracking unit.

Products: thermo gas oil (fraction 200-480°C), gases, gasoline and cracking-residue.

Temperature - 455-540 °*C*

Pressure – 100-1000 psi

Basic parameters of quality thermo gas oil:

- •Sulfur content;
- •Coking ability;
- •Fractional composition;
- •Viscosity;
- •Pour point;
- •Correlation index (!!!)

$$C_i = 474 \, d_4^{20} - 456.8 + 48640/T_b$$

$$C_i = 0,58A + 9,$$

 $A = K_0 C_0$; K_0 is the number of aromatic rings in a hypothetical raw material molecule; C_0 is the carbon content in the cyclic structure,%. •The reactor section (furnaces of light and heavy feedstock, reaction chamber);

•Section of separation of the reaction products (high and low pressure flasher, stripper, fractionation column, gas separator);

•Section of heat exchange equipment (heat exchangers, refrigerator, water cooler)

Cracking of straight run residue



1 - furnace of heavy feedstock; 2 - furnace of light feedstock; 3 - reaction chamber; 4 - high pressure flasher; 5 - separator; 6 - refrigerator; 7 - air cooler unit; 8 - fractionation column; 9 - low pressure flasher; 10 - stripper; 11 - heat exchanger.

Description of scheme

After heating in the heat exchanger 11 the feedstock 1 is entered to lower section of the fractionation column 8. Light distillate fractions are removed from the upper section of the column and directed to furnace of light feedstock 2. Heavy distillate fractions are removed from the lower section and pumped to furnace of heavy feedstock 1. Higher temperatures are used to crack the more refractory light distillate fraction. The streams from furnaces are combined and sent to the reaction chamber 3, where additional time is provided to complete the cracking reactions. Then the cracked products are separated in the high pressure flasher 4, where a cracked residue from the lower section of the flasher is entered to the low pressure flasher 9 and gas, vapor gasoline-kerosene fractions are sent to the lower section of the column 8. The gas, vapor gasoline fraction are removed from the upper section of the column and low pressure flasher 9, then they are cooled in the air cooler unit 7 and refrigerators 6 and sent to the separator 5. Gases are fed to the gas fractionation unit and gasoline is directed to stabilizer.

The cracked residue are sent from the lower section of the low pressure flasher 9 to the stripper 10, where it is exposed to distillation on vacuum thermo gas oil and cracked residue .

Apparatus	Temperature, °C	Pressure, MPa	
	Furnace 1		
entrance	390-410	5,0-5,6	
output	490- 500	2,2-2,8	
	Furnace 2		
entrance	290- 320	5,0-6,0	
output	530-550	2,3-2,9	
	Reaction chamber		
top	495-500	2,0-2,6	
bottom	460 - 470		
High-pressure evaporator			
top	450 - 460	1,0-1,3	
bottom	430 - 440		
	Rectification column		
top	180-220		
battery	300 - 330	0,9-1,3	
bottom	390-410		
Low-pressure evaporation column			
top	170-200		
bottom	400-415	0,25-0,40	
	Vacuum column		
entrance	305-345	0,007-0,01;	
top	70-90		
bottom	300-320		

Material balance of thermal cracking of straight run residue in the production of the serial I and vacuum II thermal gasoils is the following (in mass%):

	Ι	II
Gas	5,0	5,0
Vapor of gasoline	1,3	1,3
Stable gasoline	20,1	20,1
Thermo gas oil	24,2	52,6
Distillate cracking residue	48,3	19,9
Losses	1,1	1,1



<u>Thermal processes are carried out in the</u> <u>presence of catalysts</u>





<u>What is the main raw material for the subsequent</u> production of carbon black (soot)?



Name 6 basic parameters of quality thermo gas oil



<u>Choose the correct temperature of cracking of</u> <u>straight run residue</u>



THANK YOU FOR ATTENTION!!!