

The Study of the Bifunctional Catalyst Pt / Re Used in the Platforming Unit for Obtaining High Octane Number of the Gasoline

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Abstract:

The original function of the process of platforming is to develop heavy naphtha (HSRN), coming from the atmospheric unit of distillation with a weak octane number (NO = 44), to obtain a mixture of fuels a number octane raised by catalytically supporting specific groups of chemical reactions. The installation is divided into two sections: Section hydrobon. Section platforming.

The rafinat coming from the bottom of column 12C2 to feed the section platforming, is divided into two parts whose flows are controlled and mixed with gas rich in hydrogen. Bottom of the column, one obtains stabilized reformat which is aspirated by their pump to ensure the heating of the column whereas a part is sent towards storage after being cooled by the air cooler and the condenser.

In catalytic catalyst of reforming, there is voluntarily associated a hydrogenating function -dehydrogenating, brought by platinum deposited, with an acid function brought by the alumina support (Al₂O₃). The mechanism of action of this bifunctional catalyst depends on the severity of the operation, of the quality of the load and the type of catalyst.

The catalyst used in the catalytic process of reforming is a very elaborate bifunctional catalyst whose performances are constantly improved thanks to the experimental research supported on an increasingly large comprehension of the phenomena.

The American company Universel Oil petroleum (UOP) marketed several series of bimetallic catalysts such as R16, R20, R30 and R62 consisted Platinum / Rhenium on an acid support consisted the alumina added with a halogenous compound (chlorine) .

Key words: Platforming, Amelioration, Octane Number, Catalyst.

Presentation of the unit of platforming

The original function of the process of platforming is to develop heavy naphtha (HSRN), coming from the atmospheric unit of distillation with a weak octane number (NO = 44), to obtain a mixture of fuels a number octane raised by catalytically supporting specific groups of chemical reactions.

The installation is divided into two sections [1]:

Section hydrobon.

Section platforming

Section of naphtha pretreatment (hydrobon)

This section is used for the pretreatment of load HSRN (heavy Naphtha) in order to eliminate the poisons such as the undesirable sulphur, nitrogen, oxygen and compounds.

Naphtha hydrotraity of the bottom of **12D1** feeds the column (sputter) **12C2**.

A temperature equal at 130 ° C after pre-heating in exchangers 1 EA-A/Et; in the splitter, the gases of head are cooled and condensed respectively in I ' air cooler 1E6 and condenser **1E7** then recovered in the balloon 12D2 from where the liquid quantity ensures the backward flow of column heading by **12FRC5** and excess is sent towards the column of stabilization of the unit of *topping* and the gases join the system fuel-gas by **the 12PRC2**. Bottom of the column, leaves pretreated heavy naphtha called " Unifinat " of which a part ensures the rebouillage bottom of this column with control of flow ensured by regulators **12FRC6/7** the other part being

taken again by pump 12G8 to feed the section platforming

Section platforming

The tinifinat, coming from the bottom of column 12C2 to feed the section platforming, is divided into two parts whose flows are controlled and mixed with gas rich in hydrogen.

The combined load (unifinat + circulating gas) is heated initially in the exchangers then in the furnace before penetrating at the head of the engines. There as many exists rooms (03) in the furnace than of engines (**12C3, 12C4 and 12C5**), because of endothermicity of the reactions and the need for heating the effluent circulating in the engines in order to establish the same temperature at the various entries of these engines.

Column heading, leave the gases which are cooled in the air cooler and digests before their admission in balloon 12D6 from where the separate .Qn between the phases is carried out liquid (propane and butane) and gas (methane and ethane).

Bottom of the column, one obtains stabilized refomat which is aspirated by their pump to ensure the rebouillage of the column whereas a part is sent towards storage after being cooled by the air cooler and the condenser.

General information on Catalytic Reforming

Chimism of the process and mechanism of the chemical reactions

In catalytic catalyst of reforming, there is voluntarily associated a hydrogenating function - dehydrogenating, brought by platinum deposited, with an acid function brought by the alumina support (Al₂O₃). The mechanism of action of this bifunctional catalyst depends on the severity of the operation, of the quality of the load and the type of catalyst.

- **Dehydrogenation of naphthenes:** It is a very significant reaction which occurs in first engine **12C3** it makes it possible to reach a very high number of octane. It fastest of all the reactions brought into play and is led to the formation of the aromatic ones. This reaction occurs only on the metal site and it is supported by a low pressure and a high temperature; it is strongly endothermic.

Isomerization of naphthenes and paraffins

Isomerization of naphthenes

The isomerization of a cyclohexane cyclopentane is the first phase necessary for the conversion of cyclopentane into aromatic; this isomerization involves a rearrangement of the ring and alkyl-cyclohexanes change, in their turn, quickly into alkyl-aromatic by undergoing a dehydrogenation. It is held in engine **12C3**.

Isomerization of paraffins

The isomerization of light paraffins Indeed constitutes the only possible improvement of the octane number NO, one passes from NO = 62 for normal pentane to NO = 80 for isopentane.

It is held quickly under the conditions of the process in engine **12C4**. This reaction is caused by the acid function of catalyst.

Deshydrocyclisation of paraffins

The mechanism of this reaction can be schematized as follows; It is the reaction most difficult to cause: It consists of a difficult molecular rearrangement of the naphtene paraffmes: it is the phase of cyclization of a paraffin.

The deshydrocyclisation is supported by a low pressure and high temperatures. The acid functions and metal are necessary to cause this reaction. These reactions take place in engines **12C4** and **12C5**.

Hydrocracking

As its name indicates it, this reaction consists in breaking certain connections under the action of hydrogen.

Because of the isomerization of the deformed ring and reactions of formation of ring which must undergo alkyl-cyclopentanes and pressures of the load, and owing to the fact that the catalyst must have an acid function, the possibility of hydrocracking per acid promoter is large.

The hydrocraquage of paraffins is relatively fast and it is supported by a pressure and a high temperature in engine 12C5.

Demethylation

In this secondary reaction, the hydrocarbon molecule cracks by releasing a methyl under the action of hydrogen.



The reactions of demethylation can especially take place during the starting of the unit after the regeneration of catalyst because, at this time there, the function metal of catalyst is very active; this reaction can be avoided by addition of sulphur during regeneration. It is supported by a temperature and a high pressure.

Desalkylation of the aromatic ones

This reaction consists in breaking the radical alkyl connected on the aromatic nucleus under the effect of the hydrogen. Cette reaction is catalysed by the acid function and it is supported by a temperature and a high pressure; it is similar to the reaction of hydrocraquage.

Catalytic catalyst of reforming Presentation of catalyst of reforming

The catalyst used in the catalytic process of reforming is a very

elaborate bifunctional catalyst whose performances are constantly improved thanks to the experimental research supported on an increasingly large comprehension of the phenomena.

The American company *Universel Oil petroleum* (UOP) marketed several series of bimetallic catalysts such as **R16, R20, R30** and **R62** consisted Platinum / Rhenium on an acid support consisted the alumina added with a halogenous compound (chlorine).

Effect of the poisons and the agents decontaminating on catalyst

The catalysts with platinum are very sensitive to poisoning; the support can be also poisoned. Generally, the poisons and decontaminating them are divided into three classes:

Metals: These poisons damage in a permanent way the catalyst. Arsenic is most harmful; it must be present in quantity lower than 0,001 ppm in the load while lead must be in quantity lower than 0,05 ppm.

Sulphur, made up nitrogenized, water and halogens

Sulphur the maximum concentration tolerated in the load is of 0,5 ppm because the sulphur compounds cause a kinetic inhibition of the hydrogenating function of catalyst and that, by adsorption of the hydrogen sulphide H_2S on platinum, thus reducing dehydrogenation, the deshydrocyclisation without for all this isomerization and the hydrocraquage are affected.

Nitrogenized compounds: the nitrogenized compounds produce ammonia which causes a kinetic inhibition of the acid functions of catalyst like that of the reactions of isomerization, of hydrocraquage and of dehydrocyclisation.

Olefins and coke: The olefins cause the coke formation; their content must be maintained has a value lower than 2 %. coke can be considered known a poison permanent in the absence of regeneration or temporary in the regenerative steps.

Independent variables

Type of catalyst: the nature of catalyst is a true operational variable. A good catalyst must accelerate each last elementary reaction in review while limiting the parasitic formation of coke and most significant, it is to optimize the output in platformat with a good activity and stability of catalyst. The catalyst would thus have well to be chosen to be used. The choice is possible since there exists on the international market of catalysts of various basic formulas, namely the suitable level of chloride, platinum and in various agents of activation.

Temperature of the engine: it is the basic variable to control the quality of the product. The catalysts of platforming function in a broad range of temperature (430 - 520 °C); above 520 °C, the reactions thermal (cracking) occur, which cause a drop in the output in platform.

Space speed: space speed is the quantity of naphtha treated by a certain quantity of catalyst during a certain lapse of time. It expresses in volume by volume per hour (VVH) or in weight by weight and by hour (PPH).

The quality of the product (octane number) decreases with the increase space speed; to maintain the quality of the product, it would be necessary, in this case, to increase the temperature of the engines, and a very low speed space causes thermal reactions what decreases the output in platformat.

Pressure of the engine: the average pressure of catalyst is close to the pressure of the last engine since it contains 50 % of

the total quantity of catalyst. The pressure decrease makes increase the output in hydrogen and in platformat, the requirement in temperature decreases to maintain the quality of the reduced product but the lifespan of catalyst.

Hydrogene/hydrocarbure report/ratio: we saw that a significant pressure of hydrogen was necessary and very effective to avoid the formation of coke; this is ensured by the recycling of part of hydrogen produces by the formation of the aromatic ones.

The rate of recycling is generally defined like the molar report/ratio of pure hydrogen to the hydrocarbon load. The increase in report/ratio H₂ / HC improves the stability of catalyst and the flow of naphtha through the catalytic bed.

Dependent variables

Activity of catalyst: the activity of catalyst is defined as being the weighted average temperature to have a number octane of the platformat in conformity with the standards. For each type of catalyst, there are graphs giving the requirement wait according to the properties of the load.

Selectivity of catalyst: the type of catalyst, the contaminant of the load and the report/ratio water / I chloride influence the selectivity of catalyst.

Stability of catalyst: the speed to which a catalyst loses its capacity to maintain constant an output or a temperature is determined by the following variables.

Characteristics of the catalyst R62

- Bimetallic catalyst Pt / Re
- Commercial name R62 (UOP)
- Chemical composition: 0,22% in weight of Platinum.

Menouar Hanafi- The Study of the Bifunctional Catalyst Pt / Re Used in the Platforming Unit for Obtaining High Octane Number of the Gasoline

0,44% in weight of Rhenium.

- Support: Alumina Al 2 0 3 99, 34 % in weight (this support contains 0,9 % to 1,1 % in weight of chlorine).
- Charging density: 0,663
- Apparent density: 0,710
- Spherical form of diameter: 1/16 of inch.
- Total quantity of catalyst: 25276 kg.

