

Lecture №8 Hydrovisbreaking

Three visbreaking processes belong to this category:

- *Under hydrogen pressure*
- *With hydrogen donor*
- *Under hydrogen pressure, with catalyst in suspension (slurry)*

All three processes have as their purpose the fixation of hydrogen during decomposition reactions via free-radicals.

The third process uses catalysts with a weak hydrogenating activity (iron oxides). Although the process is exothermic, the products are olefinic in character. This process is in fact borderline between the thermal and catalytic processes. It has many common points with the hydrocracking processes of residues.

Visbreaking under hydrogen pressure

- The operation uses operating conditions similar to those of classical visbreaking, but under a hydrogen pressure between 80 and 180 bar.
- The flow diagram of this unit differs from the classic one by the fact that the products leaving the soaker enter a high temperature separator. The vapor phase leaving the separator is condensed and cooled. The liquid is knocked out and the gases rich in hydrogen are compressed and recycled. The system is identical to other processes that involve hydrogen treating of liquid fractions.
- The reaction order and the activation energy are identical to those for classic visbreaking. The distribution of the distillation cuts, their olefinic character, and the distribution of sulfur and nitrogen are also the same as in visbraking. The main differences are in the quality of the residues. The one from hydrovisbreaking is more stable, has a lower viscosity and a lower content of n-pentane and n-heptane insolubles.

The consumption of hydrogen is 0.2–0.4% by weight, but its action has not been yet completely elucidated. It is certain that, thermodynamically, it limits the dehydrogenation of the polycondensed naphthene-aromatics, thus reducing the formation of precursors for polycondensation. From the chemical point of view, hydrogen is taken up by acceptors. The mechanism of this action is not completely understood.

Several hypotheses have been proposed:

- Direct activation of the H–H bonds by collision with radicals in the liquid phase. It is however difficult to accept that the radicals in the liquid phase possess enough energy to dissociate the hydrogen molecule.
- Hydrogenation of the very reactive pericondensed aromatics that could act as hydrogen donor solvents.

Our more nuanced interpretation is that in the first step, interactions take place between hydrogen and the free radicals, especially methyl in the vapor phase, with the formation of atomic hydrogen. This is similar to the process that takes place in hydrolysis. The atomic hydrogen formed is much more reactive than the molecular one or the methyl radicals. Atomic hydrogen interacts with the radicals in the liquid phase and interrupts the polycondensation reactions. This hypothesis does not contradict but can accommodate the participation of the pericondensed aromatics and of the vanadium and nickel sulfides. In view of the high working pressures and of the weak participation of the hydrogen to the reaction, it is doubtful that this process will have an economic justification .

Visbreaking with hydrogen donor

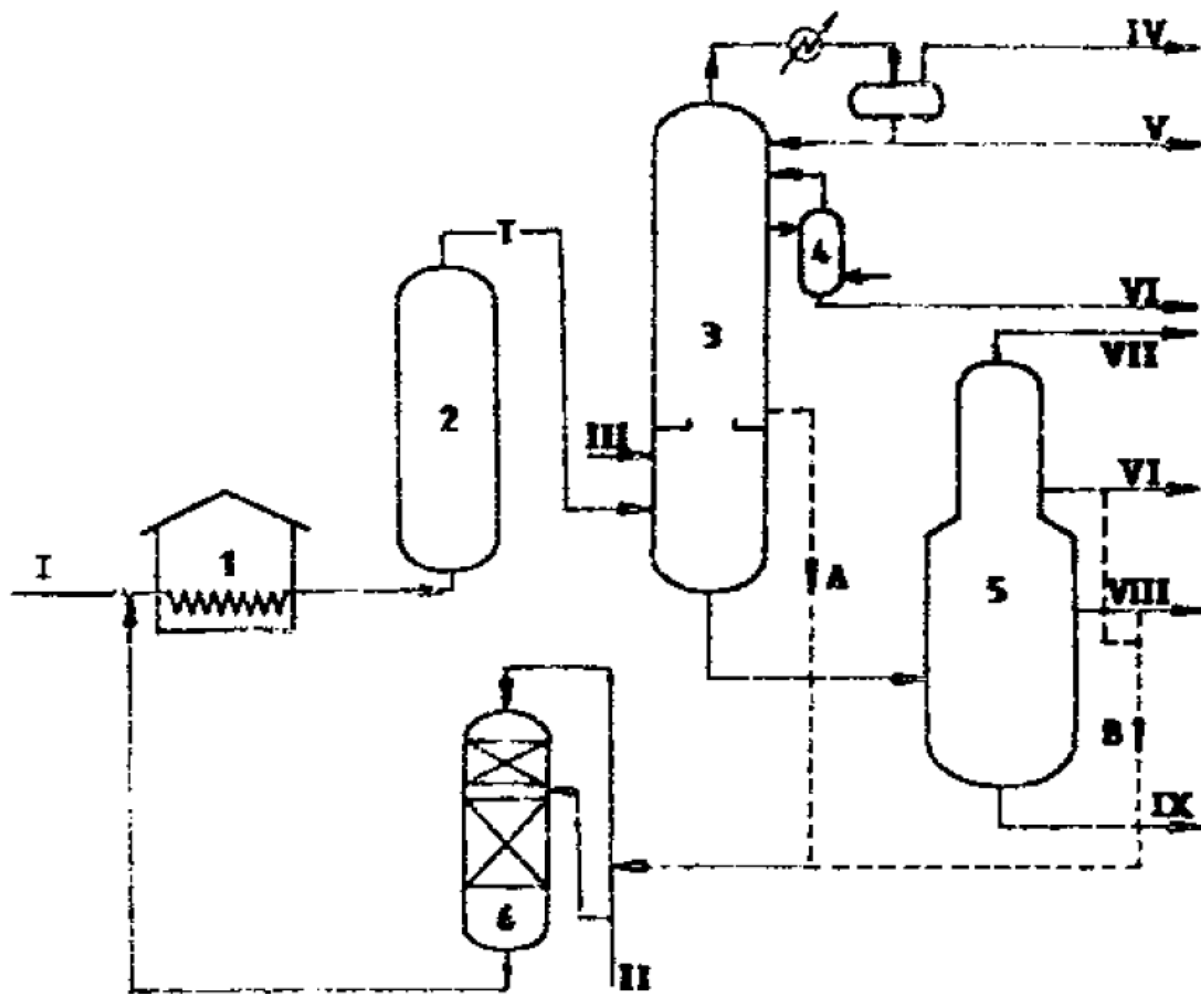
These processes are much more efficient with respect to the participation of hydrogen to the reaction, than those under pressure of hydrogen discussed above. As a consequence, they lead to larger improvements in the yields and product quality.

The process uses as hydrogen donors fractions rich in polycyclic aromatic hydrocarbons, such as: tetraline, dihydroanthracene, dihydrophenantrene, dihydropyrene etc., by themselves or in the mixtures. While in the heater and soaker, these hydrocarbons give up the hydrogen that participates in the reactions. After that, they are resubmitted to hydrogenation, which proceeds without difficulties using the classic methods.

As donor, one may use the easily available, strongly aromatic fractions, such as: the bottom product from the fractionator or the recycle gas oil from the catalytic cracking unit, the tar from the pyrolysis plants, and the tar from the coals coking.

Concerning the pressure in the furnace and soaker, it is determined by the used donor and must be enough to maintain it integrally in a liquid phase. In this way the pressure in a unit that uses a hydrogen donor does not exceed the pressure used in classic visbreaking. The retrofitting of a classical visbreaking unit to hydrogen donor operation becomes easy.

The typical flow diagram of a unit for hydrogen donor visbreaking is given in Figure.



Hydrovisbreaking with hydrogen donor. 1-furnace, 2-soaker, 3-flasherfractionator, 4-stripper, 5-vacuum column, 6-donor rehydrogenation; I-vacuum residue feed, II-hydrogen feed, III-donor, IV-gases, V-gasoline, VI-gas oil, VII-vacuum system, VIII-heavy gas oil, IX-residue; A-recycling with aromatic donors, B-recycling with polyaromatic donors.

The usage efficiency of hydrogen is very high. Only very small amounts are eliminated together with the gases of the process (about 1.4% by weight for the C1–C3 fraction). Besides the significant increase of the distillates yield in the detriment of the residue, its increased stability is especially important. This increase is explained by the interaction of the donor with the radicals present in the liquid phase, which sensibly reduces the condensation reaction. Besides, the asphaltenes contained in the feed are hydrogenated and their concentration in the final product becomes lower than in the feedstock; in some cited cases, the decrease is 25%.

Hydrogen donor hydrovisbreaking produces high yields of valuable products, operates at moderate pressure (generally below 30 bar) and uses inexpensive and readily available donors. It is expected that in the future this process will further expand and find new applications.