

A QUICK SURVEY ON THE ADVERSE CONSEQUENCES OF REFINING VISBREAKER NAPHTHA IN MIDDLE DISTILLATE HYDRO-CRACKERS

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Abstract

On the contrary to the high hydrogen partial pressure (near 200 bars) present in the middle - distillate hydro-cracker reactor, Visbreaker naphtha cannot be well refined there. Briefly speaking, three categories of adverse effects can occur as the consequences of such a refinement:

- A- Products specifications ; including mercaptan formation, considerable total sulfur content and remaining aromatic compounds in the products.
- B- Catalyst and chemical reactions; consisting of lower reactor residence time, lower hydrogen partial pressure, higher polymerization and coke formation, higher nitrogen content (and weakened cracking) and formation of dried- out points or hot spots on the catalyst bed.
- C- Hydrodynamics; including higher pressure drop for reactor heater tubes, formation of annular mist or slug flow regimes of two phase flow in the reactor heater tubes, and thermodynamic asphaltenes carry - over to the hydro-cracker reactor catalyst bed.

Key words: visbreaker naphtha, middle - distillate hydro-cracker, olefins refining, asphaltenes carry- over, two phase flow regimes.

1. Introduction

As the general intension to reduce “ bottom of the barrel” in petroleum refineries strengthens gradually, its conversion into useful products is more considered.

Obviously, the first step in this way is the optimum use of existing facilities. At least one of the scenarios acceptable during this decade for “ bottom of the barrel ” reduction consists of using the visbreaker (viscosity breaking) unit. This unit exists in many petroleum refineries and converts the crude oil vacuum distillation residue into fuel oil via a mild thermal cracking. During this process, a side product - called visbreaker naphtha - is also produced. Its amount is usually 8 to 13 volume percent of feed. Due to its high sulfur content and some other impurities, it should be refined before entering the refinery gasoline pool (Fig.1).

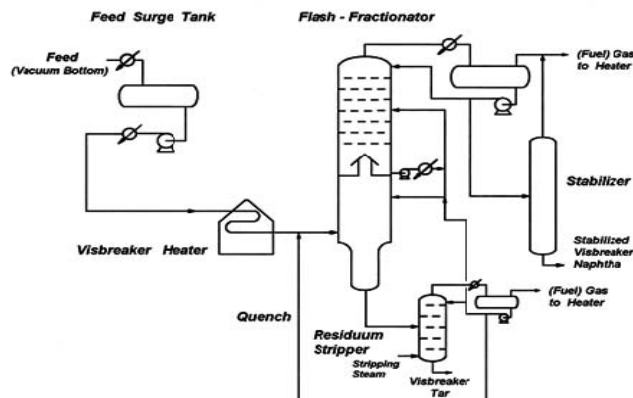


Figure 1: Flow diagram of visbreaker unit

It may appear that hydro-cracker feed stream is a suitable one for visbreaker naphtha injection. But, this is not the case, and this article explains why.

2. Theoretical Background

Today, many refineries use hydro-cracking process in one of three main types to produce :

- 1-Gasoline
- 2-Middle - distillates (kerosene, jet fuel, diesel fuel, gas oil)
- 3-High quality lubricating oils

In the second one (middle distillates producing type - Fig.2), a waxy gas oil is used as the feed stream , under the hydrogen pressure of about 200 bars at 400 °C , yet all the visbreaker naphtha impurities can not necessarily be refined under these severe conditions . The adverse effects of visbreaker naphtha injection into the hydro-cracker feed stream can be divided into three categories, which are described below:

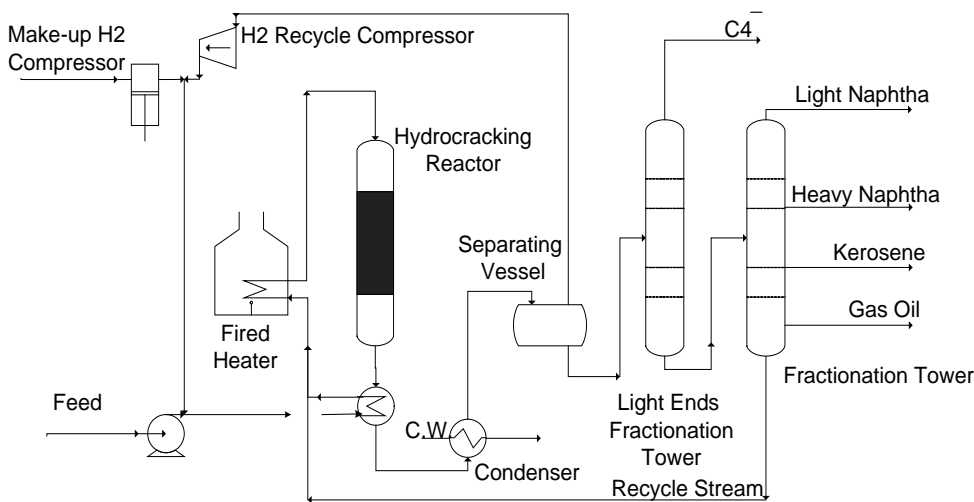
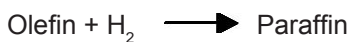
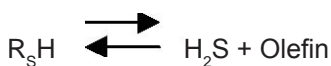


Fig. 2 - A Schematic Diagram of a Single Stage Middle Distillate Hydrocracking Unit

2.1 Products Specifications

(I) Mercaptan content - Two main impurities of visbreaker naphtha are mercaptans and unsaturated compounds (specially mono - olefins and di - olefins). In the hydro-cracking unit, they react as follows:



The first reaction occurs considerably and spontaneously at the temperatures above 343 °C. The middle distillate hydro-cracking reactor temperature is about 400 °C.

But, since the equilibrium reaction of mercaptan dissociation is faster than olefin saturation, which is a catalytic and slower reaction, some new mercaptans may be formed again, at the reactor outlet^[1,2]. This is done by the reverse side of the first reaction, and with the concentrated H₂S evolved during hydro-desulfurization reactions. This is called the mercaptan returning reaction. If all the visbreaker naphtha olefins are not completely saturated before leaving the reactor, mercaptan formation will definitely occur. This is realized by a positive " Doctor test " for each product specially, during the " end of run " period of the catalyst, this phenomenon can make some product specifications unacceptable.

2.2 Catalyst and Chemical Reactions

(I) At reactor conditions, about 25% of the (middle distillate) hydro-cracker feed evaporates. Where as all the visbreaker naphtha injected evaporates and expands a lot, which severely reduces the residence time for the reactor contents, and also the hydrogen partial pressure. The consequences of this fact would either be incomplete refining reactions, or the necessity for feed reduction of the unit, to keep the products qualities high enough.

(II) Poly-nuclear aromatics (PNA's) can do many reactions with each other and with olefins. Consequently, condensed

aromatic associations and finally coke, will form. This coke formation tendency is increased by increasing the aromatic associations sizes [1,5]. In other words, the olefins in visbreaker naphtha tend to form coke with the aromatics in the hydro-cracker feed.

(III) The nitrogen present in the feed molecules, disturbs the hydro-cracking reactions by forming ammonia, because it reduces the catalyst acidity [5,7,8], and deactivates the active sites (of course, in amorphous catalysts). Injection of visbreaker naphtha; not only increases this nitrogen content, but also reduces the reactor residence time, via its evaporation. Therefore, the products qualities will become lowered, unless the hydro-cracker (fresh) feed rate is reduced [1,6].

(IV) By visbreaker naphtha injection, the overall feed vaporization increases roughly from 25 %volume to 33 %volume. Therefore, some problems of dried out points or hot spots formation may arise on the catalyst bed, due to mal-distribution of liquid or low heat capacity of vapor with respect to liquid. All these problems can be quite harmful for the catalyst and also intensify coke formation on it.

2.3 Hydrodynamics

(I) As previously mentioned, after visbreaker naphtha injection, the reactor charge heater tubes pressure drop is increased. By maintaining the upstream pressure constant, the feed stream flow rate and the production rate would decrease. Or, to keep the feed rate constant, the upstream pressure should be increased, which may have limitations in some plants.

(II) By the considerable amount of feed vaporization after visbreaker naphtha addition to the fresh feed, the two phase flow regime inside the reactor charge heater tubes will shift up most probably to annular mist or slug flow. In the first case, the tube skin temperature may drastically increase, which is dangerous for such severe operating conditions. In the latter one, very high pressure drop, severe mechanical vibrations and metallurgical damage will occur, due to successive heating and cooling effects of moving slugs inside the heater tubes (Fig .3).

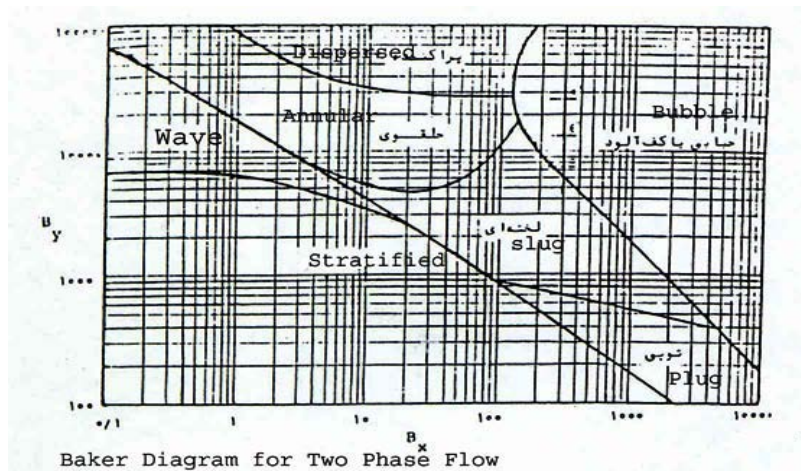


Fig. 3 - Baker diagram for two phase flow [9]

Generally speaking, such a considerable change in the heater charge should be studied in advance, to prevent the aforementioned phenomena.

(III) Three types of asphaltenes and polymerization precursors carry over may occur from the visbreaker unit fractionating tower to the hydro-cracker catalyst bed:

1-Carryover caused by fractionating tower upsets or floodings. This can be prevented by proper design, operation and control of the flash fractionating tower.

2-Mechanical entrainment of very tiny liquid droplets into the gas stream leaving up each fractionation tray, in the tower. This can be avoided by proper installation of mist elimination pads inside the fractionation tower.

3-Thermodynamic carryover of heavy compounds (even asphaltenes) along with the lighter ones, up the fractionating tower. This even occurs during the normal operating conditions of the tower. Prevention of such a case requires some modification in the tower, to improve its fractionation quality-.We have designed such modifications via a special simulation of tower operation.

In all these three cases, excessive coke formation and even catalyst deactivation may occur in the hydro-cracking reactor.

3. Experimental Results

(I) The following table shows this effect in a refinery, during its “middle of run ” period of the hydro-cracker catalyst:

Table 1 -Doctor test results for hydro-cracking products, before and after visbreaker naphtha injection^[3]

	Light Naphtha	Heavy Naphtha	Kerosene (Jet Fuel)	Diesel Fuel
Before B.N. injection	+	-	-	-
After B.N. injection	+	+	+	+

(II) The total sulfur in the recycle feed stream to the reactor should be reduced from (e.g.) 12 000 ppm in the fresh feed to 270 ppm. whereas, after the visbreaker naphtha injection , it only reduces to 5 300 ppm. H₂S at low concentrations can prevent aromatic rings saturation, which can increase the gasoline octane number and decrease the jet fuel smoke point. High H₂S concentrations reduces the cracking activity of the catalyst^[6].

(III) Jet fuel and illuminating kerosene should contain the minimum feasible amounts of aromatic rings, to have high cetane number and smoke point, respectively. The main step in the aromatic ring opening is its (hydrogen) saturation^[1,7], which is an equilibrium reaction^[4,7]. Therefore, olefin saturation reactions will reduce it, as a competitive reaction.

As a specific case, the aromatic content of a hydro-cracker kerosene product increased from 14 volumetric percent to 20.9 volumetric percent, by visbreaker naphtha injection during the “ middle of run ” period of the catalyst . Hydro-cracker kerosene is mostly used in jet fuel production. Again, the above phenomena can raise some problems during the catalyst “ end of run ”period. Also, unnecessary catalyst change may happen, if not considering the above points.

4. Conclusion

As described above, Visbreaker naphtha injection into the middle distillate hydro-cracker feed stream, is in no case a simple, straight - forward way for its refining. Several adverse consequences may arise from such an action, and is not recommended.

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