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EFFECTIVE PARAMETERS OF PNA REDUCTION IN VISBREAKER NAPHTHA

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Abstract:

Visbreaker naphtha (a by-product in petroleum refineries) can be further refined and blended into motor-gasoline .The first step of its refining is distillation, to fine-tune its boiling range. But, extra-ordinary care is necessary to eliminate its polynuclear aromatics (PNA) content, which is environmentally harmful. Some of these hydrocarbons are toxic and carcinogen , therefore their content must be reduced until allowable range.

In this article, the visbreaker unit distillation tower was simulated to evaluate effective parameters on PNA separation. According to the obtained results, polynuclear aromatics content can be reduced to less then 1 ppm with modifications in the distillation tower and system upgrading.

Keywords: *visbreaker naphtha, modifications, polynuclear aromatics reduction*

THEORETICAL BACKGROUND

By gradual global depletion of petroleum reservoirs, the price of it and its derivatives will also increase. Therefore, it is necessary to attain its optimum use via upgrading its by-products. There is a petroleum refining process called viscosity breaking (Visbreaking), which produces fuel oil via mild thermal cracking of crude oil vacuum distillation residue. Figure (1) shows a schematic diagram of the actual plant considered in this study.

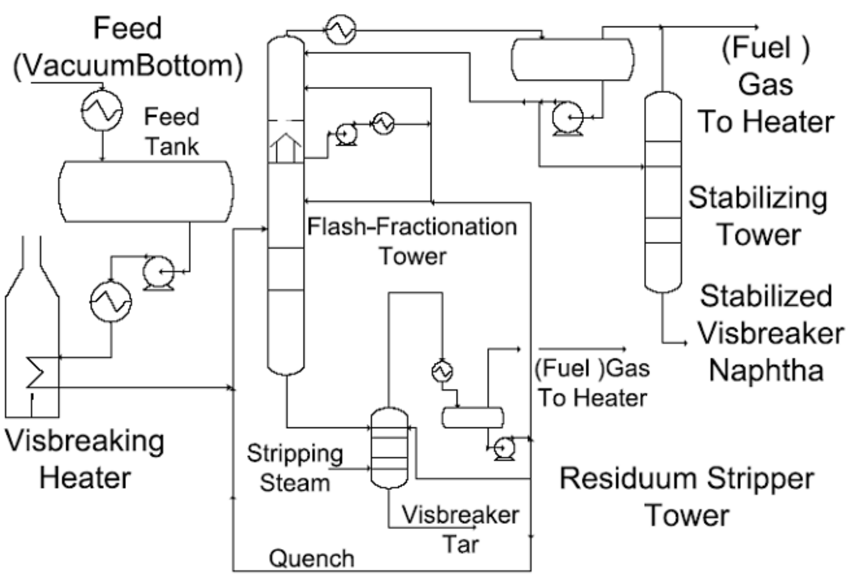

Figure (1): Visbreaking Unit

It also produces a by-product (visbreaker naphtha), which can be added to motor gasoline, after proper refinement. To do so, the first step is the adjustment of its boiling range by distillation, during which the elimination of environmentally harmful impurities should be considered. This requires suitable modifications in the existing visbreaker distillation column, and is the theme of the present study. Certainly, such an approach can be used in similar cases. Visbreaker naphtha is produced as the overhead liquid product of the visbreaker unit fractionation tower (8 – 13 volume % of the unit feed).

This liquid by- product is in many cases burnt as a steam boiler fuel. But, using it as a motor gasoline constituent requires the elimination of its Polynuclear Aromatics, polymerization precursors (mainly poly diolefins), asphaltenes and high sulfur content compounds. Polynuclear Aromatic Hydrocarbons are hydrocarbons with multiple unsaturated (condensed) ring structures and are commonly referred to as PAHs or polynuclear aromatics (PNAs). Some of the compounds within this class of pollutants are considered mutagenic, which has led to restrictions on their release into the environment. PAHs find their way into air, water and soil in a variety of ways, but the major source is the incomplete burning of fossil fuels. The burning of coal in power stations or petrol (gasoline) in cars, trains and trucks leaves a residual tar and is the primary cause of PAHs in densely populated areas. As such, there is a need to be able to detect PAHs in the environment. Particular attention is paid to the separation methods.

Aromatics containing 11 to 22 carbon atoms are among most toxic and dangerous environmental pollutants .For example benzo(a)pyrene and benzo(a)anthracene are carcinogen or mutagen (figure 2).

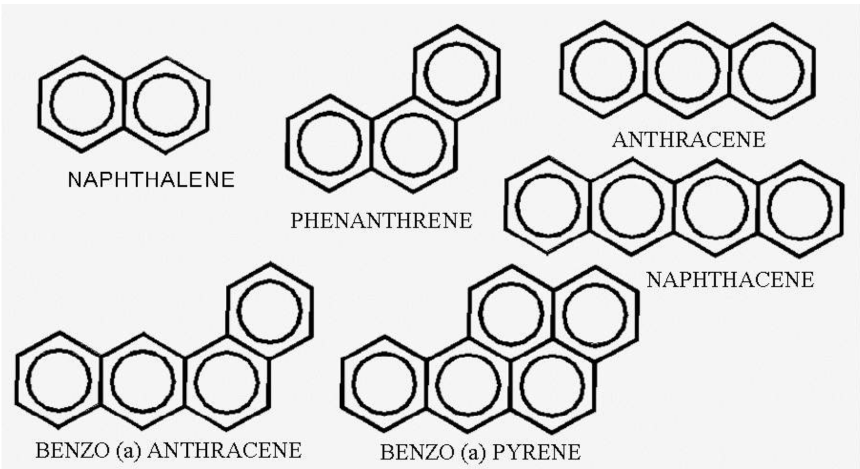

Figure (2): Some of poly-nuclear (polycyclic) aromatic hydrocarbons

Although natural petroleum fractions (in contrast to coal liquids) show very low mutagenic activity (due to the extensive alkyl substitution of aromatic rings in petroleum materials), any observable mutagenic activity was associated with the neutral fraction from column chromatography, containing poly aromatic hydrocarbons or neutral heterocyclic molecules of nitrogen, sulfur and oxygen. Higher boiling molecules have very low (acute) toxicity. In other words, the worst case is for the parent aromatic hydrocarbons and heterocyclic ones[1,2] . One way of PNA elimination is hydro de-aromatization (HDA), taking place at high hydrogen partial pressures, catalyst contact and considerable temperatures. Although, this way is usually costly, the aromatics cannot be completely saturated, unless at very severe conditions. For example, in an Arabian Light vacuum gas oil, after 70 bars HDA , 31 wt.% and after 140 bars HDA , 9.6 wt.% of aromatics remain[3]. Another simple – yet efficient – way is distillation, if done properly.

The presence of the aforementioned impurities at the distillation tower top section can occur via 3 ways[4] :

- **Flooding in the tower.** This can be prevented by a proper tower hydraulic design and operation.
- **Asphaltenes mechanical carry-over.** Such a case is less effective than the previous one, and can be eliminated by installation of good mist eliminators in the column.
- **Asphaltenes presence, due to the thermodynamic equilibrium.** In this situation, asphaltenes are carried up the column, just like the "heavy key" components of feed, via

thermodynamic equilibrium .In other words, this phenomenon is an intrinsic property of the feed, and is not due to the malfunction of the tower.

Experimental tests and simulation

There are a number of tests, which can measure the aromatics. Refractive index (RI), ultraviolet (UV) and aniline point can be used as quick indicators of aromatics content. However, their absolute values are meaningful only when the test results for a given sample have been previously correlated with a more definitive test method [5]. The (IP-143) experiment is for determination of asphaltene and resin content of petroleum and petroleum cuts (topped previously to 260°C).

The (IP-346) method determines the polycyclic compounds in unused lubricating base oils and asphaltene free petroleum fractions (boiling points around 300°C). None of the last two tests exactly fits to visbreaker naphtha.

Other tests (accessible to us); gas chromatography (GC), GC-Mass and NMR (nuclear magnetic resonance) methods were also considered. But, the obtained PNA spectra were appeared within the spectral span of other hydrocarbons. Then, 98 volume % of a 20 liter visbreaker naphtha sample was distilled (TBP Distillation method ASTM D-2892), and heavy contaminants were concentrated in the black residue. Doing the (IP-143) experiment on it, showed the (qualitative) existence of asphaltene and resin content in this residue .To obtain an idea about the amount of heavy impurities present in visbreaker naphtha, the TBP distillation was applied to it up to 190°C (to eliminate all naphtha type constituents).

The weight of this very heavy residue was determined accordingly as 200 ppm in the (original) visbreaker naphtha.

It is necessary to improve the fractionation performance of the existing column, to produce a standard light fuel (figure 1).

The tower has 14 actual trays and a flash evaporation section. According to the tower mechanical diagrams, the only useful empty space for this purpose is its flash zone (with about 5 meters height). By using an efficient packing zone, the fractionation ability of the tower can be enhanced considerably. Among the aforementioned impurities, PNA can be thought of as the most harmful one.

This is because of having the least molecular weight and highest volatility, which penetrate them into the visbreaker naphtha cut, at the tower top. Therefore, the PNA measurement in this cut can be used as a quantitative tool for monitoring the effectiveness of packing application.

In order to have a heavy- key component in the tower simulation, the Asphaltene - PNA mixture was represented by a pseudo- mixture of light PNA s. Naphthalene ($C_{10}H_8$) is the lightest PNA. Considering the final boiling point of visbreaker naphtha (about 185 °C), and the high volatility of naphthalene (with 2 aromatic rings), another heavier PNA should be mixed with it. Therefore, some 3 and 4 aromatic rings compounds (anthracene, phenanthrene or naphthacene) were concentrated on. naphthacene and heavier PNA compounds have very low vapor pressures (much less than naphthalene and phenanthrene)[6]. Table I shows some of their properties[7-12].

Table I – Some Properties of Poly-Nuclear Aromatics

PNA	Molecular Weight (g/mole)	Boiling Point (°C)	Vapor Pressure (torr)	No. of Rings
Naphthalene	128.16	217.95	0.082	2
Phenanthrene	178.23	338	1.250E-4	3
Anthracene	178.23	340	5.63E-6	3
Naphthacene	228.29	440	8.28E-7 mmHg @ 20 °C	4
Benz(a)anthracene	228.29	434.85	2.2E-8 mmHg @ 20 °C	4
Benzo(a)pyrene	252.3	310 - 312	5.25E-9	5

Therefore, a naphthalene - phenanthrene mixture was assumed as the representative of all PNA s. Moreover, all the heavy residue (200 ppm) was attributed to this pseudo- mixture. This means that this study is at the safe side, with respect to the PNA reduction. Table II shows the TBP of visbreaker naphtha sample.

We used the PRO II simulation software for system modeling[13]. One point in the application of the commonly used process simulation software is that they use characterization distillation assays (ASTM D-1160, TBP, etc.) for hydrocarbon cuts, which can not directly be used to trace the small amounts of PNA in the proposed cut .To overcome this problem, two feed streams (PNA mixture and the main tower feed) were defined for the tower. Now, the absolute amount of the mixture and also the ratio of the naphthalene to phenanthrene in pseudo - mixture are unknown (in fact our adjusting parameters or degrees of freedom). Therefore, two specifications (200 ppm of PNA in naphtha and the ratio of visbreaker naphtha rate to the tower products rates) are defined to complete the simulation.

Table (II): TBP of Visbreaker Naphtha Sample

ASTM D 86		TBP (ASTM D 2892)
Volume %	Temperature (^oC)	Temperature (^oC)
IBP	27.5	55.0
10	51.5	80.0
30	80	96.2
50	108	113.1
70	131	129.9
90	155	147.3
FBP	185^+	165.3^+
Total sulfur content	8484 ppm	

First of all, the existing situation was simulated. Then, by studying the required changes in the column internals (using a packed zone), it was realized that the impurities of visbreaker naphtha could be reduced to less than 1 ppm.

Discussion and Results

Existing operating conditions do not show any cases of flooding or mechanical carry-over in the (existing) column under study (flooding factor = 59.6 -77.5%). Table III summarizes the simulation results.

As previously stated, the aforementioned impurities are eliminated better than the pseudo-mixture used; due to their heavier molecular weights and higher boiling points. In other words, by using the properly selected type of packing in the tower, the need for construction of a second fractionating column can be overcome. Also, the existing mid-side cut of the tower (its mid-reflux withdrawn from the chimney tray) was used to wet and wash this packing surface and achieve a satisfactory mass transfer; therefore no extraneous equipment installation was required.

Table (III): The Results and Required Modifications of Tower

The pseudo – mixture:

Composition: { 1 wt. % Naphthalene; 99 wt. % Phenanthrene }

Concentration in Visbreaker Naphtha: { before modifications 200 ppm; after modifications < 1 ppm }

Mass Flow Rate (in the tower input) : 272.4 Kg / h

Packing Zone:

Theoretical Trays Equivalence:	4
Height:	1.83 m
Internal Diameter:	2 m
Packing Size:	2.5 cm (nominal diameter)
Type:	Ceramic Intalox Saddles

As can be seen, the packing bed height is not too much and by using the remaining flash zone empty space, having a more efficient fractionation or lower cost packing types is also possible.

Considering the aforementioned topics, the following results can be concluded:

- In many cases of having serious difficulties in the application of analytical methods, the problem can be overcome by some proper and simplifying engineering assumptions. In other words, many complex chemical mixtures can be simulated by properly selected components.
- By gradual tightening of environmental protection regulations, using high-performance tower internals is a good choice in modifying existing columns, instead of costly construction of new ones.
- As the petroleum price increases, having a new look at the existing facilities is both economically and environmentally beneficial.

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