ADDITIVE FOR VISBREAKING: AVB-95

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Key Words: visbreaking, additives

SUMMARY

The primary goal for visbreaking is reducing the viscosity of heavy feedstocks by means of a mild thermal breakdown so it may possible to produce fuel oils, as well as to prepare the load for subsequent catalytic breakdown. The major operating costs of this process are strongly dependent on two factors: diluent consumption needed in the fuel oil formulation, and plant's coking rate resulting from the severity of the treatment. Some additives available on the market are specifically designed to exert a counteraction against the coking tendency of the heavy feedstocks inside the furnace tubes; and they, to a greater or lesser degree, accomplish this task. These commercial additives performance was evaluated and compared to that of an additive package, based on several mechanism of action, recently developed by Instituto Colombiano del Petróleo (ICP). As a result of the pilot plant experiments and field trials, it was found that the new additive considerably reduces the quantity of diluent necessary for fuel oil preparation; and moreover, the run time is increased with less plant maintenance requirements.

INTRODUCTION

The visbreaking process is a mild thermal cracking process wherein vacuum residues and asphalt are processed in order to prepare the feedstock for FCC and to reduce the viscosity of these loads to produce fuel oil (1-3).

Among the reactions taking place in the visbreaking process we have:

- Side-chains from resins and aromatics are broken leading to further decrease in the average molecular weight, and consequently reducing their peptizizing capability.
- Free radicals are reacted to form asphaltenes.
- The asphaltenes are subjected to dealkylation and dehydrogenation reactions whose products are more difficult to peptizize, causing the colloidal system destabilization and asphalting precipitation.
- The saturated components (paraffins) are split into shorter, non-polar compounds which facilitate asphaltene precipitation.

These undesired reactions are responsible for the main drawbacks and limitations in the run time and severity applied in visbreaking operations. This is why we rely on additives (4-7) to avoid the aforementioned problems.

MATERIALS AND METHODS

Three commercial additives already tried at an industrial scale were chosen for evaluation on a visbreaking pilot unit built by the ICP (Figure 1). Besides, the heavy residues used in the experiments came from Ecopetrol's refinery in Barrancabermeja, and had the physicochemical characteristics sketched in Table 1. The operating conditions set up were 870°F (465°C), and 25 minutes residence time.

The working mechanism for these latter additives is based on the formation of a protective film over the tubes metallic walls at the prevailing operating conditions, but they do not act upon the system stability. At the beginning of the run the surface temperature is around 870°F (465°C) and becomes slowly increased with time as the coke layer starts to deposit, forming an insulating barrier. The evaluation at pilot scale showed that, coincidentally, the additive having the best performance was the one being used at the Ecopetrol's plants at that time. It was also observed that said commercial additives were not effective as operating temperatures were over 884°F (473°C), maybe due to product decomposition.

This clear disadvantage of available commercial additives led us to think about developing new additives working under mechanisms, different from that o film-forming, such as: hydrogen transfer, metal passivators, and fee radicals scavengers. As a result we obtained a package of additives having a higher protective efficiency against coking than commercial products, as it is seen in Figure 3.

RESULTS

With the available additive used by the Cartagena Refinery, acceptable gas, nafta and gas-oil performance was obtained, which was increased by the application of the AVB-95 additive. These differences are shown in table 2.

Benefits from the application of AVB-95

Although performance of the commercial additive being used in the Cartagena refinery was considered satisfactory from the standpoints of gas, naphta, and gas-oil yields; a remarkable increase in these variables output was seen once the AVB-95 was applied. The additional benefits are clearly depicted in Figure 4.

1. *Profit due to VBN (viscosity blending number) increase*
Depending on the severity and the additive dosage, an increase in VBN from 1.0 to 2.5 points is easily reached. It should be carefully considered that a single point increase in VBN for a plant that processes vacuum residues means total savings of about KUS $800 per year.

2. Savings with maintenance
Due to a more porous and softer coke formation caused by the additive action, maintenance work on the furnace and the fractional towers is made easier, and cost noticeably reduced. These savings equal to KUS$220 per year.

In the Cartagena refinery the average coke film thickness within the furnace tubes was reduced in almost 1.5 cm. The coke deposition rate in the fractional towers was also lowered and its smooth consistency allowed an easier removal.

3. Increase in the service factor
For run #37 at the Cartagena refinery, an increase in the service factor of 76% was registered due to a greater operating time equivalent time to 9 days a year. The benefit was then around KUS $583 per year.

4. Versatility in operation
Through the use of this additive it may be possible to obtain a reaction product having a lower asphaltene content and greater distillate production, which at the same time permits operating at the same severity levels for longer run times. These latter condition bear an increase in conversion without risking the stability of the fuel oil or coking the furnace.

5. Product performance
The Cartagena refinery plant used a commercial additive and for this reason the action of additive AVB-95 is not compared with an actual target, but additional benefits are readily achieved over the commercial additive (See Table 2). .

Through the addition of the new additive we were able to increase the conversion by 1.52%, specially in nafta production, by 0.71%, but also in gas-oil, by 0.81%.

The analysis of saturate, aromatic, resin and asphaltene content (SARA) of the visbreaking tars shows a broad change in the distribution of each family as a result of the free radicals caping action and the increase of hydrogen concentration in the system foreseen by the anti-coking agent AVB-95.

The average changes in composition for the visbreaked resids are:

Saturates: increased by 1.21%
Aromatics: increased by 10.0%
Resins: decreased by 8.9%
Asphaltenes: decreased by 3.0%

This new chemical distribution improves the VBN in the visbreaking tar, allowing the operating plant a severity similar to previous runs, increasing run time due to a lower quantity of asphaltenes in the system, hence producing less coke. As a secondary effect there is an increase in the conversion of nafta and gas-oils, operating at the same severity.

CONCLUSIONS

With the use of AVB-95 there are the followings benefits:

- Increase in the ΔVBN of the tars.
- Less coke production in the furnace and run time increases.
- Easy removal of the coke.
- More conversion.

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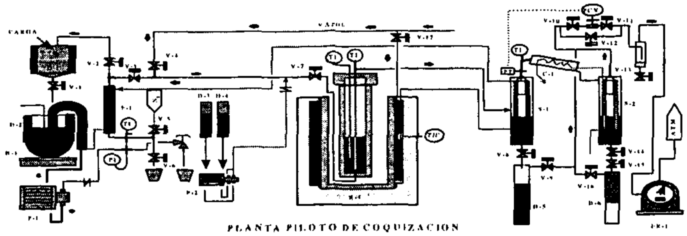
Table 1. Characterization of visbreaking loads

Property	Vacuum residue	Demex residue
Density , 15,6 ºC	0.989	1.08
Sulfur, %w	2.26	2.32
Conradson Carbon, %w	18.98	31.5
Penetration, 25 ºC, 1/10 mm	2.8	0
Softening point, ºC	57	91
Ni, ppm	119	195.1
V, ppm	343	403.7
	2.3	-2.1

Table 2. Performance with additives

Additive	Commercial	AVB-95
Load, BPD	20.000	17.000
Fraction	Output, % wt	Output, % wt
Gases	3.90	3.68
Naphta	5.45	6.16
Gasoil	34.36	35.17
Residues	59.00	57.60
Conversion	39.80	41.32



PLANTA PILOTO DE COQUIZACION

B-1- celda de carga, D-1- embudo de carga, D-2 - tambor de carga, D-3- tambor de aditivos, D-4- tambor de aditivos, D-5- tambor de fondos, D-6- tambor de naftas, S-1- Separador de naftas y gases, S-2- separador de gases, E-1 y E-2 *intercambiadores*, C-1- condensador, FR-1- medidor de gases, P-1 bomba de carga, P-2 bomba de aditivos, H-1- horno de viscorreducción.

Figure 2. Evaluation of commercial additives

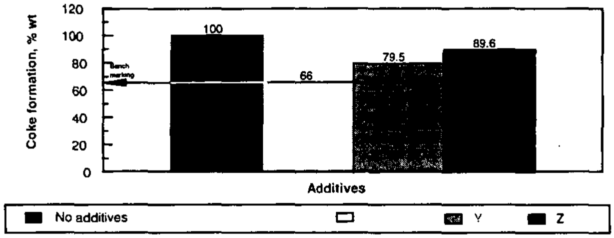


Figure 3. Evaluation of additives developed by the ICP

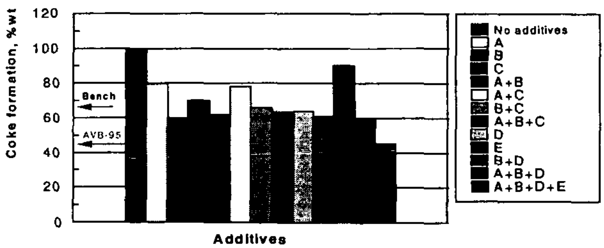


Figura 4. Benefits from the use of the AVB-95 additive in visbreaking of vacuum residue