CONTROL OF SEVERITY IN VISBREAKING

J.A. Carrillo*, F. Pantoja*, G. Garzón*, H. Barrios, J. Fernández**, E. Carmona*** and J. Saavedra*****

*-ECOPETROL-Instituto Colombiano del Petróleo; **-ECOPETROL-Cartagena Management; ***-ECOPETROL- Barrancabermeja Management.

Test results of the behavior of different feeds in the visbreaking process at the pilot as well as the industrial plant level are presented, in agreement with their insoluble matter content in nC_7. The interval studied was 10%m (vacuum barrel bottoms) at 32%m (deasphalted barrel bottoms). In the processing of barrel bottoms, a correlation was found between the abrupt change in the slope of efficiency in function of severity by temperature (at the 745-760 °K interval) regarding the change in slope of the line of stability determined by means of the Merit Test, while at the interval tested for residence time (3.8-6.4 minutes) there was no change in slope found. In the processing of deasphalted barrel bottoms, no correlation was found between the abrupt change in the slope of efficiency in function of the severity by temperature (at the 749-773 °K interval) regarding the change in slope of the line of stability determined by means of the Merit Test, while at the interval of residence time tested (5-13 minutes) a change of slope was found in the Merit Test. In this type of feeds, it was observed that the severity is controlled most efficiently by temperature, without noticeably increasing coke production in the oven, while for barrel bottoms, it is preferred to control severity by means of residence time. The study shows the influence of steam and light cycle oil on the processing of DEMEX barrel bottoms in visbreaking.

In addition, correlations are shown between the Merit Test, the Coking Index using Heithaus and the Stability Factor of the feeds and products.

INTRODUCTION

Visbreaking is a process of thermal breaking of barrel bottoms that is carried out between 748-773 °K, with a residence time (in the reaction zone) of 6-10 minutes. Sometimes from 1 to 4% v of steam and from 0% to 10% of light cycle oil (LCO) is introduced.

Visbreaking is a low capital investment process and is operated at threshold conditions to produce a greater quantity of distillates and reduce the quantity of diluent used in the preparation of fuel oil from visbroken tar. The severity threshold has been studied by several researchers (Savaya, et al., 1988) and it is determined by the stability of the fuel oil and the quantity of coke deposited on the inner walls of the oven. To measure severity in the operation, techniques such as the Merit Test, the Coking Index using Heithaus (John and Adam, 1999) and the Stability Factor (S.F.) which relates oil composition to severity (Kuo, 1984).

Another important factor that limits severity measured in function of conversion is the quality of feed. The greater the quantity of insoluble matter in nC7, greater will the production of barrel bottoms be and the less the production of gas-oil (John and William, 1982).

For this study, only the coil visbreaking technology was considered, because this is the technology of the plants currently operating in ECOPETROL refineries.

EXPERIMENTAL

Simulations at the pilot level were carried out at a plant built in ECOPETROL-Instituto Colombiano del Petróleo (Carrillo and Pantoja, 1998).

The stability of the visbroken residue is determined by means of two tests developed by the IFP (Merit Test) and the WRI (Heithaus Titration Test); which consist of a paper chromatography and the precipitation of asphaltenes with i-octane, and are based on the solubility of the sample to be analyzed in a blend of aromatic and paraffin solvents of known proportions.

For the tests, asphaltenes were obtained from the deasphalted vacuum bottoms of the oil blend of the Barrancabermeja refinery (insoluble matter in n-C7 between 30 and 35%m) and vacuum bottoms of oil blend from the Cartagena refinery whose characteristics are given in Table 1.

Heithaus parameters of severity

Titration using Heithaus consists of taking a constant quantity of a visbroken barrel bottom (2 g) and diluting it in three different volumes of o-xylene: 5, 7 and 9 ml respectively. These concentrations are titrated with isooctane. The methodology is included in Schabron and Pauli.

Table 1: Characteristics of Vacuum Bottoms

Properties/Refinery	Barranca-Bermeja		Cartagena			Standard/equipment
Typo of bottom feed	DEMEX		Vacuum			
nC_7 insolubles, % wt	32.7	30.5	11.9	13.48	16.45	UOP-614
Saturates, % wt	4,0	2,7	11.2	10.8	11.2	Iatroscan Method
Aromatics, % wt	44,4	47,9	56.5	55.9	49.7	Iatroscan Method
Resins, % wt	34,2	33,0	24.1	23.5	28.3	Iatroscan Method
Asphaltene; % wt	17,5	16,4	8.2	9.7	10.8	Iatroscan Method
CCR, % m	38.8	36.5	22.2	22.46	24.53	ASTM D-4530
Merito test	—	3.0	5.0	4	4	IFP
F.E.	0.5	0,8	0.32	0.33	0.28	*
Density @ 15 °C, gr./ cm^3	1.077	1.0892	1.0196	10.254	1.0256	ASTM D-70
Viscosity @ 150 °C, cP			229	421	588	ASTM D-445
VBN	-12,8	-5.2	2.69	1.94	1.03	

* -Calculated by Kuo, 1984. F E = (Aromatics + Resins) / (Saturates * CCR)

Coking index

This index is defined as the peptizabilitation (Pa)/dilution concentration (Cmin) ratio. It is based on the considerations that Pa decreases when the parameter of solubility or the molecular weight of the asphaltenes is increased, and Cmin increases when residue stability decreases. Preliminary studies suggest that a ration near one (1) indicates a highly stable system ratio and coking begins when the ratio is near 0.3.

RESULTS AND DISCUSSION

1. Processing of vacuum barrel bottoms

1.1 Evaluation of severity based on temperature

Product efficiency for the different conditions of severity used, does not vary noticeably for temperatures below 754 °K (figure 1). For temperatures above 754 °K, coke formation is triggered and a drastic reduction in the production of barrel bottoms occurs, which reflects in the increase of gas-oil efficiency (atmospheric + LGO + HGO) and the production of gases and gasoline.

When the content of asphaltenes, resins, coke and some of their correlations are related, similar trends are observed, where the behavior of the asphaltenes that have a maximum of 756 °K stands out, while the resins and the resin/asphaltene ratio shows an opposite behavior. These trends indicate that once the maximum cracking temperature is reached for each feed, the system stops being stable, the miscellar structure is destroyed and the asphaltenes become coke precursors. This instability is confirmed by the Merit Test performed on the visbroken tar, where a change in slope at 754 °K is observed, as is shown in figure 2. At values below this temperature, the visbroken tar is stable, while at higher temperatures the colloidal state is thrown off balance.

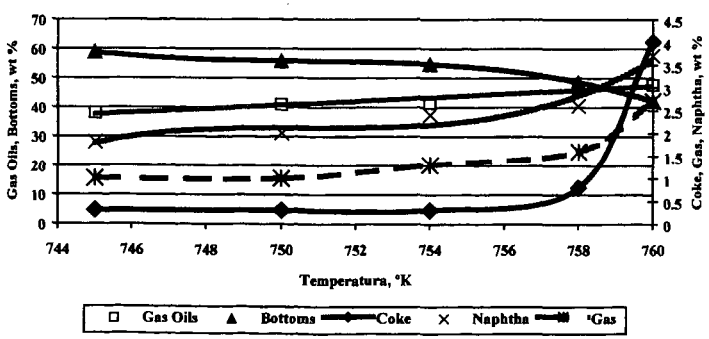


Figure 1. Severity as temperature function

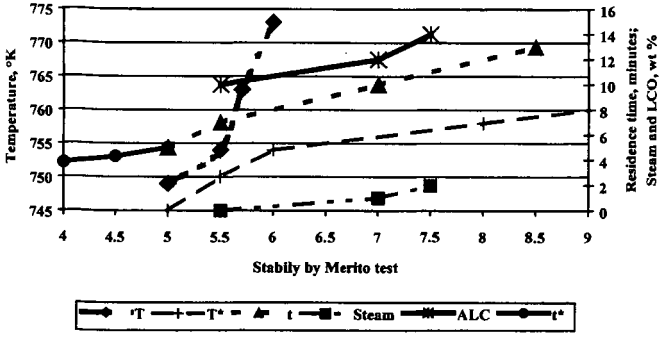


Figure 2. Stability of the visbreaking bottoms by Merite test

1.2 Evaluation of severity based on residence time

At the conditions analyzed there were no abrupt variations in the efficiency of the products. The gases, gasolines, gas-oils and coke are increased in a constant fashion with the increase in residence time, while the production of tar and the resin asphaltene ration is reduced at the same interval analyzed. The resin/asphaltene ratio is greater than that of the data with temperature variation, which explains the greater stability of the visbroken tar. This stability is shown in figure 2, where it is observed that all the values are equal to or below 6 on the Merit Test; in addition there are no changes in slope.

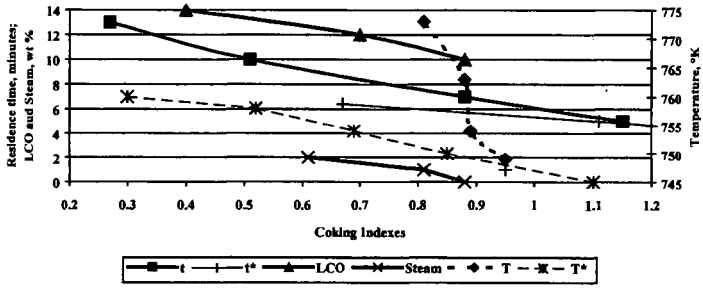


Figure 3. Coking Indexes using The Heithaus Titration and Asphaltene Solubility. Barrancabermeja Refinery

1.3 Correlations between the method of measuring the stability of the visbroken tar by means of Titration using Heithaus with the method based on the Merit Test

Figure 3 presents the titration results for different samples corresponding to variations in severity by residence time and temperature. Similarly, diagrams for steam and light cycle oil were obtained.

When the coking index is illustrated in function of severity by temperature, it is found that the recommended stability interval (0.3 - 1) does not correspond to this type of feed with the results of efficiency (figure 2) and with the Merit Test for the same evaluation. These values indicate that at a temperature of 756°K, there is a transfer from a stable area to an unstable area above this temperature. For this reason, the results seem to indicate that for this type of feed, the control interval to be recommended in the Coking Index should be 0.6-1.

A similar procedure was followed with the samples corresponding to the variation of severity by residence time.

When the modified interval of the Coking Index (0.6-1.0) is the same as in the Merit Test, all the points analyzed are within the stable interval, which supports the fact that the residence time at the interval analyzed shows less risk than the temperature in handling severity.

2. Processing desasphalting bottoms.

2.1 Evaluation of severity based on temperature.

Severity in funtion of temperature was evaluated maintaining residence time constant at 7 min, the LCO at 10% and the amount of steam supplied to the feed in 0%.

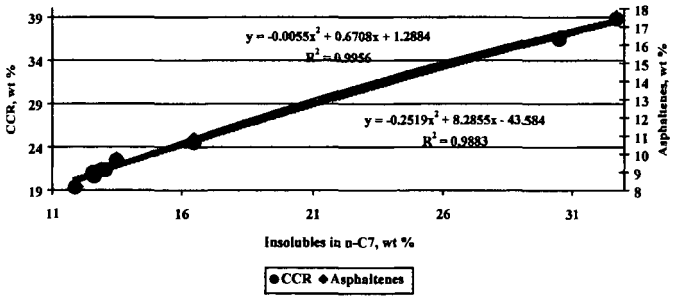
In spite of this, the system remains colloidally stable, being that the amount of resins increases and at the same time the asphaltenes decrease, becoming coke as was stated previously. Therefore, all the points analyzed by the Merit Test yield values below 7. This indicates that in the processing of this type of feeds the threshold is not found in the stability of the products, but in the amount of coke deposited on the inner walls of the oven pipes.

2.2 Evaluation of severity based on residence time.

Severity in function of residence time was evaluated keeping temperature constant at 763 °K. This value corresponds to the temperature used at the Barrancabermeja refinery. The LCO percentage was kept at 10%v and the amount of steam supplied to the feed before entering the reactor at 0% v.

Product efficiencies vary noticeably for different conditions of severity used in function of residence time, above all during periods of over seven minutes. With an increase in residence time, the production of gases, gasolines and coke is increased and the production of barrel bottoms is reduced. Just as the influence of the change in severity in function of temperature, it is expected that the increase in severity will increase the production of gas-oils, for which the production of tar would be below that illustrated. With a residence time of 7 minutes, a change is observed in the slope of coke and tar production, which coincides with the change in slope of the stability index as well as residence time. With a residence time of 13 minutes, the system is totally unstable.

The resin/asphaltene ratio shows a slight tendency toward increase as residence time is increased. It would be expected that in this order, the stability of the system increase. Nevertheless, over ten minutes of residence time, the system is unstable possibly due to the abrupt reduction in viscosity or due to the great amount of gas-oil formed in the reaction, which by dilution destabilizes the colloidal system.



2.3 Severity in function of the percentage of steam.

For these tests, residence time (7 min.), the percentage of LCO (10% V) and temperature (763 °K) are kept constant.

This variable was kept in mind due to the fact that at the Barrancabermeja refinery, the steam is used to reduce the residence time inside the furnace.

It would be expected that by increasing the percentage of steam in the feed, the residence time would be reduced and therefore soften conversion. However, the opposite is observed. When the percentage of steam in the feed is increased, the gasoline production is increased considerably and tar production is reduced drastically. This is due to the fact that the steam helps to decrease the partial pressure of the heavy fragments, improving the distillation process, or perhaps it is a hydrogen donor in the different thermal reactions that take place inside the reactor. Within this explanation, it would be expected for coke production to be reduced, which does not occur in practice, possibly due to a change in the flow rate into two phases. It can also be observed that

the coke has a constant increase with the increase in the amount of steam and that its values are above 1% m, which is a high value and implies rapid oven coking. In spite of the fact that according to the Merit Test (figure 2) the system is within the limits of stability, a change is observed in slope for concentrations above 1% m. The quality of the visbroken tar goes through a process similar to that of the tar coming from the visbreaking of vacuum bottoms as can be seen in figure 4.

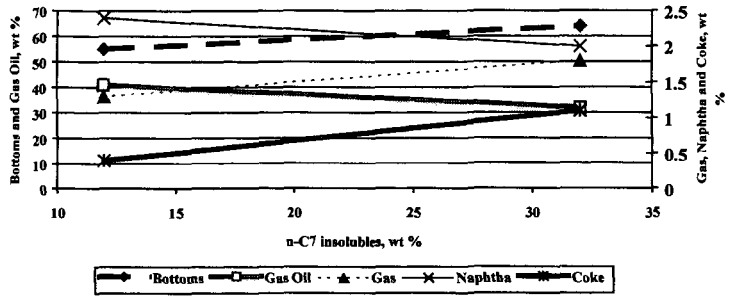
2.4 Evaluation of severity in function of the amount of LCO in the feed.

For these tests, residence time (7 min), temperature (763°K) and the amount of steam (0%) were kept constant.

Analyzing the parameters of severity in agreement with the titrations using Heithaus, it is observed that in these tests the temperature has more incidence on the stability of the visbroken star than on residence time.

To apply the corrected value of 6 instead of 0.3 on the stability threshold of Titration using Heithaus we find that the residence times of over 9 minutes give an unstable product which corresponds to two points of the interval analyzed.

In agreement with the Titration using Heithaus, values of over 12% m of LCO in the feed produce instability in the visbroken tar. The stable values in this product in agreement with the Merit Test indicate that up to 14% m of LCO in the feed is allowed. Nevertheless, this same test indicates that there is a change in slope at concentrations of 12% m, which corresponds to a value of 7 on the Merit Test. The point of the change in slope coincides with those registered for the influence of steam and residence time, which indicates that this type of feed should have not 7.5 but 7 as a control of stability on the Merit Test.



The crackability of feeds is a function of the amount of asphaltenes in it, expressed by means of the amount insoluble in C5 or C7. As this amount increases, the conversion decreases.

CONCLUSIONS

- The most important characteristic defined by cracking of a feed in visbreaking is the amount of asphaltenes it has. The higher the concentration of asphaltenes in the feed, the lower the crackability.

- For DEMEX barrel bottoms, in which the insoluble matter in nC7 are greater than 18% m, the variable that influences operational control most is temperature, which allows increases of up to 758°K reducing the production of visbroken tar by almost 4% m, the ΔVBN increases by 0.3 points and the coke increases by 22% m. At these conditions, the °API remains constant.

- With this same type of feeds, the steam as well as the ALC show similar behavior. It is recommended to use steam between 0.4 and 0.6%m, which means a reduction in tar production by 1% m and in increase in ΔVBN by 1 point and the °API by 0.4 points. Coke production is increased by 16%m. Above 0.6% m of steam, coke production can put the duration of the run at risk due to oven fouling.

- The ALC has a marked influence on the operation, which is why stricter control is recommended.

- For vacuum barrel bottoms, with concentrations of insoluble matter in nC7 below 18% m, the variable that allows the most control of severity is residence time, while for feeds with asphaltene concentrations of over 18% m, the variable that allows better control is temperature.

- The Merit Test as well as the Coking Index characterize visbreaking results well from the visbroken tar stability viewpoint, but not for the oven fouling, especially for feeds with over 18% m insoluble matter in nC7. Nevertheless, the Coking Index is more exact, which is why it is presented as a better tool for operational control.

Literature Cited:

CarrilloJ.A., Pantoja F., Barrios H., Estrada C., Alvarez N. And Chinchilla M. 1999. "Pressure control in vacuum towers". CT&F, Vol. 1 Núm. 5:25-34.

Savaya Z. F., Al-Soufi H.H., Al-Azawi I and Mohamed H.K. 1988. "The effect of Visbreaking conditions on the stability of some Iraqui Long Residues". Fuel Science and Technology INT'L., 6(3):354-366.

Maketta, Jhon and Cunnigham, William, 1982. "Encyclopedia of chemical processing and design", Ney York, Marcel Dekker

Kuo, C, J., 1984. "Effect of crude types on Visbreaking conversion". Oil & Gas Journal (Sept24):100-102.

Schabron J.F and Pauli A.T. 1999. "Coking Index using The Heithaus Titration and Asphaltene Solubility". American Chemical Society, National meeting and exposition program, Anaheim, C.A. (March 21-25): 187-193.