Evaluation of additives to reduce SOx emissions in FCC commercial units

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1. Purpose

To study FCC unit SOx emission reduction of an FCC unit located in the Caribbean, through the use of a catalytic SOx transfer additive, specifically Grace's Super DESOX® FCC Additive.

2. Introduction

Coke burned in the regenerator contains roughly 5-10% of the sulfur contained in the feed to the reactor. This sulfur is emitted by the regenerator flue gases into the atmosphere in the form of sulfur oxides (SOx).

Of all sulfur entering into the FCC, 45-50% leaves the reactor as H_2S, 5% in the gasoline, 20-30% in the LCO, and 20% in the HCO/slurry. The rest of the sulfur, on average of 5-10%, ends up in the coke [1].

In order to calculate the SOx concentration leaving with the regenerator flue gas, it is necessary to know the amount of sulfur in the coke. The amount of sulfur in the coke is dependent on the sulfur in the feed and the type of feed. The type of sulfur compounds in the feed determines where the sulfur ends. Sulfur incorporated in aromatic structures has a higher tendency to end up in coke than for instance paraffinic sulfur compounds, which are likely to be cracked in the riser and produce H_2S.

Hydrotreated feeds have lower sulfur content than straight run feeds, but the ratio $\mathbf{S_{coke}/S_{feed}}$ is higher than for straight run feeds [1]. This can be explained by the fact that during the hydrotreatment of the feeds the easily crackable, more paraffinic sulfur compounds will be cracked, leaving the more difficult and heavier aromatic compounds in the feed. These sulfur compounds will preferably end up in the coke and HCO/Slurry.

The objectives of this study in the commercial FCC unit were:

- To define the SOx emissions range in the FCC unit.
- To study the effect of feed composition and operating conditions in the SOx emissions.
- To prepare the base case and the FCC unit for the commercial evaluation of the Super DESOX® additive.

- To evaluate the effect of the Super DESOX® additive in the reduction of SOx emissions.

3. Development of the work and results

3.1 Base Case Definition

Considering that feed of the FCC unit has different components, it is important to study the effect of feed composition in the SOx emissions, several test runs were conducted during August and September 2008 and January, February 2009.

3.2 Feed component Analysis

The following FCC feed components were sampled and sent to GRACE for complete physicochemical characterization:

- Combined feed sample
- Furfural Extract sample
- Straight run VGO
- Flash Distillate (Visbreaking VGO)
- MHC feed (feed to the Mild Hydrocracker Unit)
- MHC Product (Mild Hydrocracker product)

According with the feed properties (Table 1) the less crakeable feed is the furfural extract, due to its lower API, higher sulfur, higher Conradson carbon, and Refractive Index. These analyses are related with the higher aromatics content. The calculated properties (Table 2), also shows that the furfural extract has the highest aromatics content and the lowest saturates concentration.

The highest correlation Index [2] is related with the type of hydrocarbon in the feed. According to this property, the furfural extract, the flash distillate and the MHC feed can be classified like naphthenic-aromatics feeds. The straight run VGO and the combined feed can be classified like naphthenic feed, and the MHC product like naphthenic-paraffinic feed. The quality of the feed is related with the hydrogen content and with the amount of saturates concentration, where highest values are the more crackable feeds with higher valuable products yields.

The MHC process removes 90% of the sulfur, 80% of the concarbon, 95% of the vanadium, and 100% of the nickel. At the same time the hydrogen content increases 6%, which is related with the 7.8% increase in the amount of saturates, which should improve the yields of gasoline and LPG and reduce the effect of the feed in the heat balance.

Table 2 (calculated properties) includes the conversion at the maximum gasoline point and the gasoline yield at that point. These values are related with the chemical composition of the feeds, and they are calculated using internal, under development, GRACE correlations.

Table 1. Physicochemical Properties of the FCC feed and components

Feed Name Feed Number	MHC Feed F08-2246	MHC Product F08-2247	SR VGO F08-2249	Flash Destillate F08-2250	Furf. Extract F08-2251	Comb. Feed F08-2248
API	18.92	23.69	21.28	20.33	16.21	22.05
Specific Gravity	0.9407	0.9118	0.9262	0.9319	0.958	0.9215
K Factor	11.55	11.79	11.71	11.54	11.66	11.75
Refractive Index	1.5233	1.5068	1.5150	1.5206	1.5385	1.5126
Average Molecular Weight	381	367	388	357	454	383
Arom Ring Carbons Ca, %wt	24.8	19.9	22	25.1	29.5	21.5
Napthenic Ring Carbons Cn	21.8	24.4	21.2	20.8	15	22
Paraffinic Carbons Cp, %wt	53.5	55.7	56.9	54.2	55.6	56.5
Sulfur, %wt	2.058	0.208	1.55	2.094	2.237	0.987
Conradson Carbon, %wt	0.45	0.09	0.34	0.47	0.92	0.19
Ca, ppm	0	0	1	0.2	0.4	0
Ni, ppm	0.2	0	0.4	0.3	0.2	0.1
V, ppm	1.5	0.1	2.2	1.9	1.7	0.8
Na, ppm	0	0	1.7	0	1.5	0
K , ppm	0	0	0	0	0	0
Mg, ppm	0	0	0.2	0	0.1	0
Cu, ppm	0	0	0.1	0	0.2	0
Fe, ppm	1.9	0	2.8	0	3.3	0.2
Distillation, IBP, ℃	238	198	176	264	341	178
Distillation, 5%	313	287	293	312	384	297
Distillation, 10%	337	313	326	329	403	327
Distillation, 20%	369	346	375	354	432	366
Distillation, 30%	392	372	400	373	454	390
Distillation, 40%	414	393	420	391	475	412
Distillation, 50%	436	414	439	411	496	431
Distillation, 60%	457	436	458	432	515	451
Distillation, 70%	479	458	478	455	537	473
Distillation, 80%	507	485	502	482	565	498
Distillation, 90%	551	524	538	522	611	537
Distillation, 95%	595	561	574	562	658	575
Distillation, FBP , ℃	693	664	676	667	734	681

Table 2. Calculated Properties of the FCC feed and components

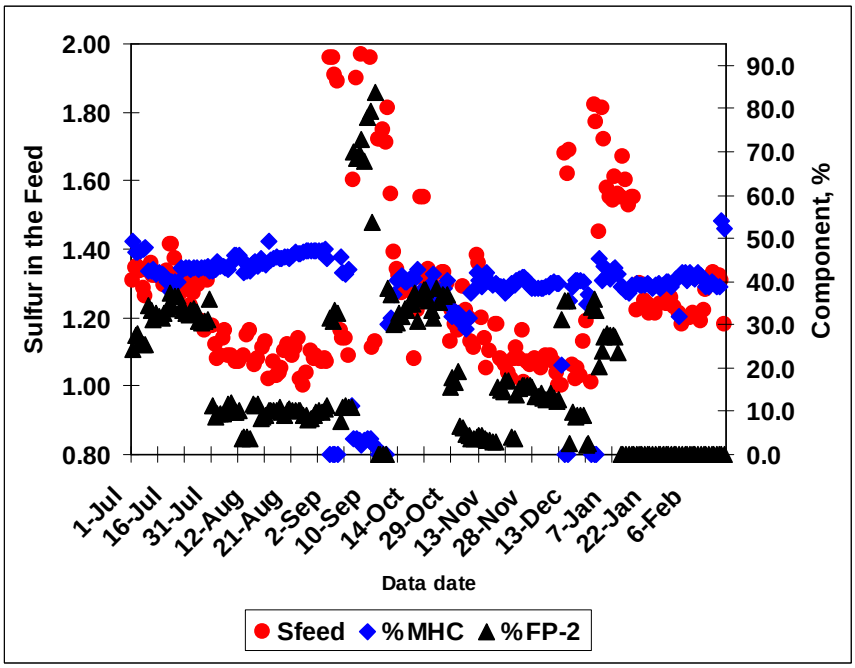
	Calculates Properties					
	MHC Feed	MHC Product	SR VGO	Flash Destillate	Furf. Extract	Comb. Feed
MeABP, ℃	439	416	436	418	500	432
MeABP. ℃	712.0	689.3	709.2	691.0	773.2	704.6
Correlation Index	57.12	45.68	50.52	55.03	59.91	48.75
Hydrogen Content, %m	12.02	12.79	12.47	12.16	11.82	12.59
Saturates, %m	45.66	53.42	49.84	46.91	44.10	51.09
Aromatics, %m	49.58	41.45	45.25	48.32	51.12	43.92
MonoAromatics; %m	27.61	28.12	28.78	28.26	26.31	28.68
Diaromatics, %m	20.73	12.62	15.57	18.93	23.39	14.42
Triaromatics+, %m	1.24	0.71	0.90	1.12	1.43	0.82
Conversion Max Gasoline; %m	73.12	78.92	76.36	73.11	69.34	77.31
Gasoline Yield, %m	48.97	54.19	52.18	49.22	45.58	52.99

The feed components with the highest contributions to the SO_x emissions are the furfural extracts and the flash distillates, which are sent totally to the MHC unit. The operation of the MHC is another condition that affects the SO_x emissions.

3.3 Feed Quality

It is well known that one of the most important variables that effects SOx emissions from an FCCU is the feed quality, specifically the amount of the sulfur in the FCCU feed. Figure 1 illustrates how the feed sulfur content in the FCC unit can vary between 1.0 %wt and 2.0 %wt S, with the most typical values being between 1.0 to 1.2 %wt S.

Figure 1. Sulfur Content in FCCU Feed (JUL08 – FEB09):



The highest feed sulfur values (1.5 - 2.0 %wt S) were obtained when the MHC (Mild Hydrocracking) unit was shut down and/or was not operating at its normal severity. This was the case during 02-10SEP2009 when the MHC product was not directed to the FCCU. During January 2009, even though the MHC feed represented about 40% of the total FCCU feed, the MHC unit was operating at low severity. For this reason, the level of sulfur in the feed increased to between 1.4-1.8 %wt S. According with equation 1, which was developed in order to predict the sulfur in the feed as a function of the FCC feed components, the FCCU feed components with the higher effect on overall FCCU feed sulfur are the VGO from the FP-1 and FP-2 units and the amount of MHC feed. Figure 2 shows a good correlation and permits one to predict the amount of sulfur in the feed using the equation 1, where the amount of each feed stream is expressed in % of the total feed.

Feed Sulfur, %wt = 2.4599 -0.01034* %FP 1-0.0064* %FP 2- 0.021* % MHC **Eq. 1**

Figure 3 and equation 2 show a good correlation between the sulfur in the feed and the API gravity. Figure 3 also confirms that the sulfur in the feed can vary between 1.0 - 2.0 %wt S. The most common values range between 1.0 - 1.4 %wt S, which correspond to an API of between 21.0 – 23.0°API.

Figure 2. Prediction of Sulfur in FCCU Feed

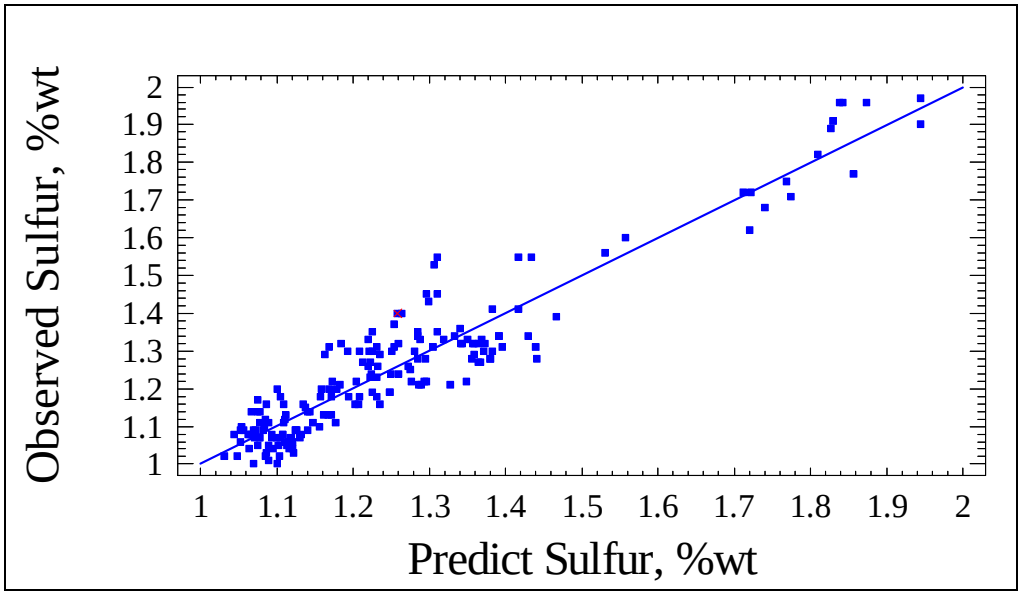
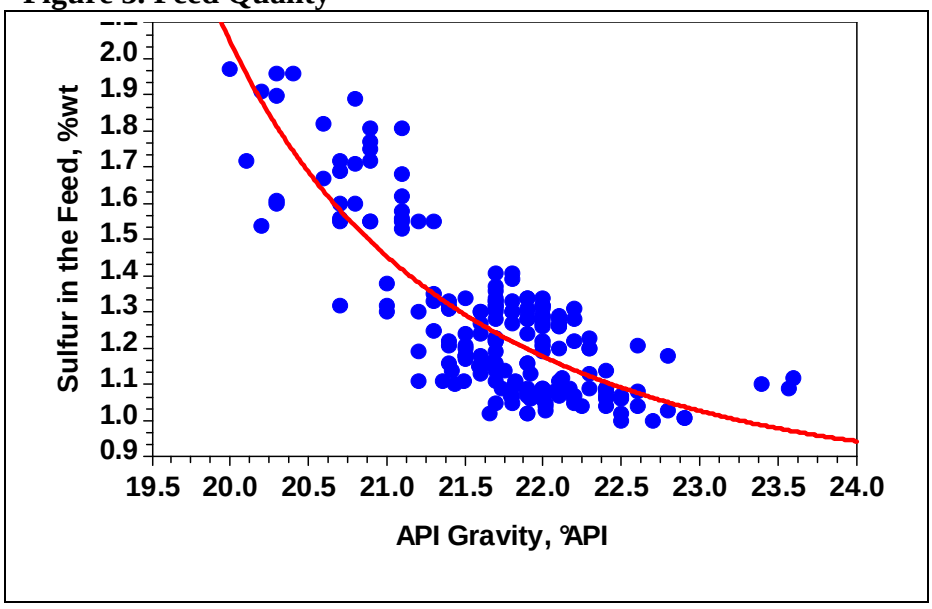


Figure 3. Feed Quality



$$\text{Feed sulfur, \%wt} = 1/ (-11.3965 + 0.97076 \times API - 0.0188 \times API^2) \quad \textbf{Eq. 2}$$

3.4 SOx emissions

As was mentioned before, the main objective of this work was to define the SO_x emissions at different operating conditions, especially with changes in feed quality. For this reason, during August 2008 and February 2009, the uncontrolled and controlled SOx emissions were measured using a portable analyzer. Figure 4 permits one to conclude that SOx emissions in this FCC unit are between 600 ppm to 1400 ppm.

Considering that the portable analyzer only measures the amount of SO_2 in the flue gas, and that sulfur in the coke is burned in the regenerator to a blend composed [3] by 90% SO_2 and 10% SO_3, it is necessary to include in the calculation the amount of SO_3, in order to have the total SOx emissions.

Figure 4. SOx emissions of the FCC unit

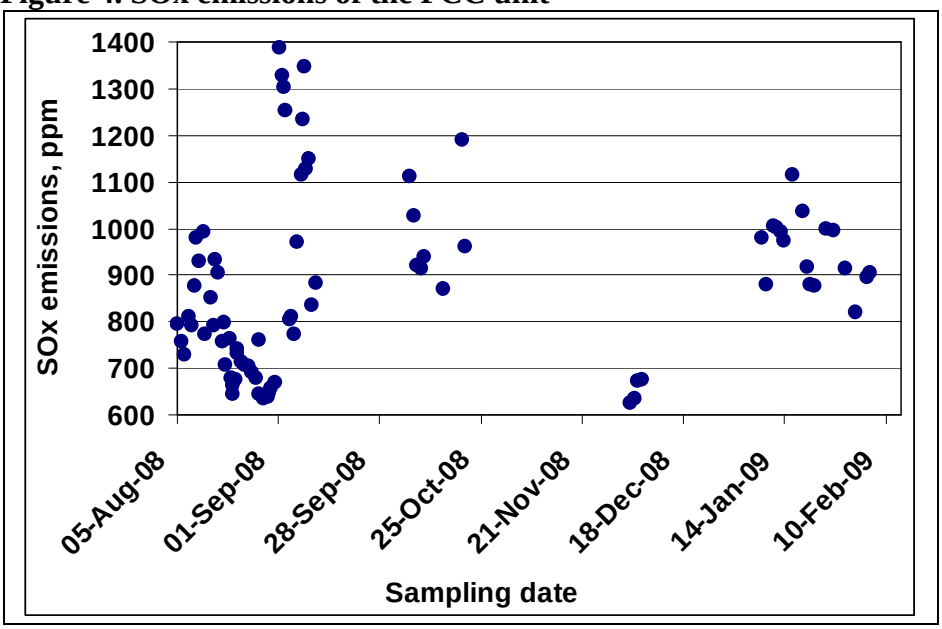
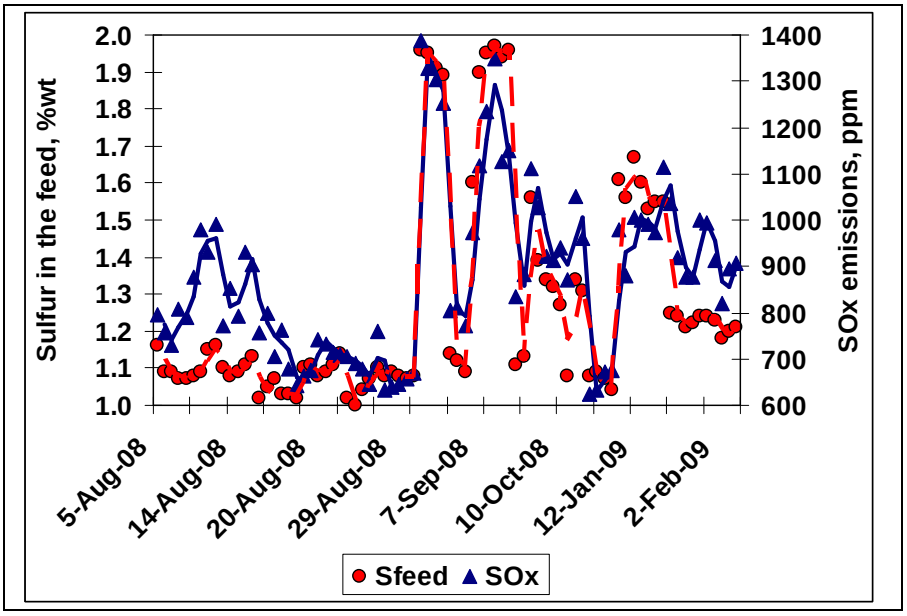


Figure 5 shows the effect of the feed sulfur in the SOx emissions. This figure permits the following conclusions:

- For feed sulfur values between 1.0-1.3%wt the SOx emissions should be between 600-850 ppm.
- If the feed sulfur values are between 1.3-1.6 %wt, especially when the MHC unit is operating at low severity, the total SOx emissions increases to values between 850-1100 ppm.
- Finally, if the sulfur in the feed is higher that 1.6%wt, especially when the MHC unit is shut down, the SOx emissions increases to values higher than 1100 ppm.

Figure 5. Effect of the feed sulfur in the SOx emissions



3.5 Prediction of SOx emissions

The FCCU SOx emissions are related to the amount of sulfur in the coke, which is dependent upon the sulfur in the feed. According to the literature [4], the ratio of S_{coke}/S_{feed} varies from 1.2 to 2.8 considering the different types of FCC feeds. The lowest values of S_{coke}/S_{feed} correspond to straight run vacuum gas oil and the highest to hydrotreated long residue (Atmospheric tower bottom).

Since it is not possible to measure the sulfur in the coke (Scoke); it is necessary calculate it using the measured SOx emissions, according to the following reaction:

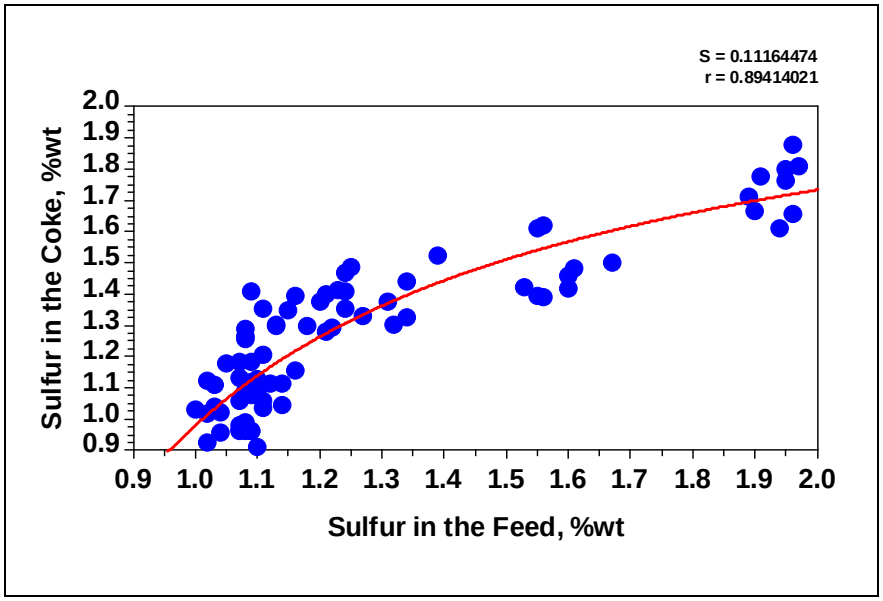
$$Scoke + O_2 \rightarrow SO_2 + SO_3$$

This reaction is produced in the regenerator and is O_2 dependent. Figure 6 shows the sulfur in the coke, calculated from the SOx emissions as a function of the amount of sulfur in the feed (Sfeed); this plot is represented by equation 3.

$$\text{Sulfur in the Coke, \%wt} = 1.721634 + 0.11275*Sfeed - 0.8531/Sfeed^2 \qquad \textbf{Eq. 3}$$

Equation 3 is a valuable tool for the refinery personal; since it permits one to calculate the sulfur in the coke using the easiest and most common analyzed FCC feed property. The sulfur in the coke and the SOx emissions are also related with the striping efficiency. The heaviest hydrocarbon feed, which is at the same time the fraction with the higher sulfur content, has to be removed and cracked efficiently in the reactor and in the striping, in order to reduce the hydrogen in the coke (Hcoke) and the amount of hydrocarbon burned in the regenerator. This affirmation is demonstrated in equation 4, which is representing in figure 7.

Figure 6. Sulfur in the Coke as a function of Feed sulfur

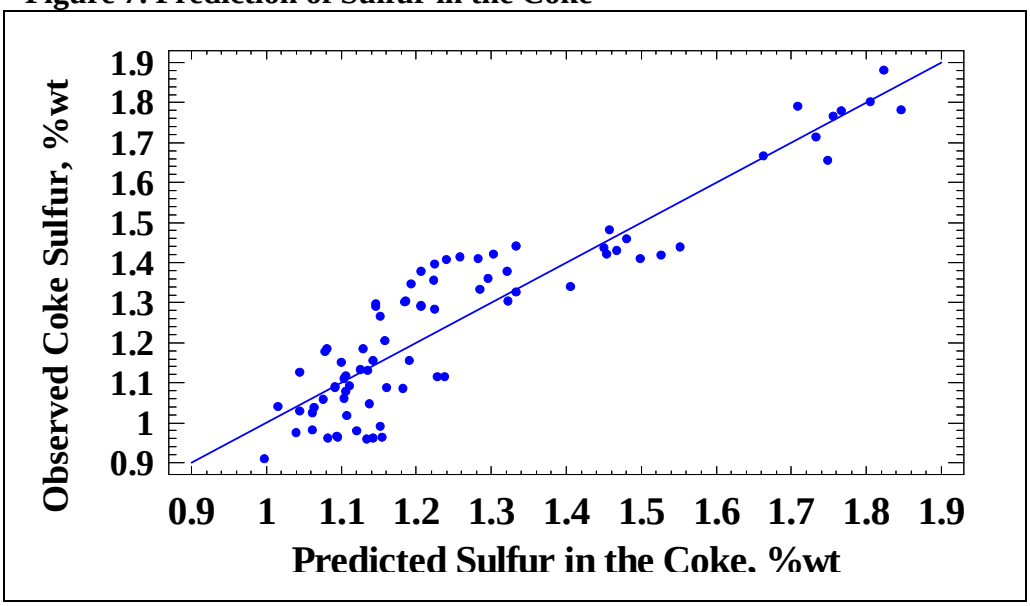


In conclusion the sulfur in the coke is also dependent on the sulfur in the feed and the hydrogen in the coke, which is related with the striper operating conditions.

Sulfur in the Coke, %wt = 1.20886 + 0.674094*Sfeed - 0.167199*Hcoke

Eq. 4

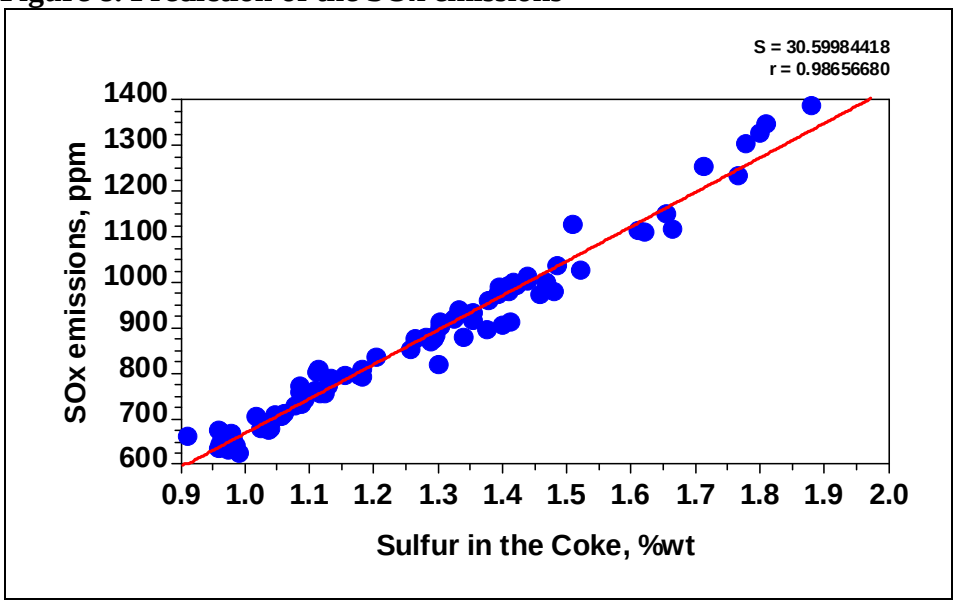
Figure 7. Prediction of Sulfur in the Coke



Knowing the amount of sulfur in the coke, it is possible to predict and to calculate the SOx emissions. Figure 8 and equation 5, show that the SOx emissions are a direct and linear ratio of the sulfur in the coke. Equation 5 is the other very important correlation for the refinery personal, since it permits the calculation of the uncontrolled SOx emissions. The uncontrolled SOx emission is important to calculate when determining the SOx reduction during the addition of the SOx reduction additive.

SOx Emissions, ppm = -86.7664 + 756.202*Scoke **Eq. 5**

Figure 8. Prediction of the SOx emissions



3.6 Super DESOX® effect in the FCC unit

In the FCC process, catalyst circulating between the oxidizing atmosphere of the regenerator and the reducing atmosphere of the reactor makes the transfer of sulfur via a SOx transfer catalyst possible. To be cost effective, the additive must trap SOx in the regenerator and release it as H_2S in the reactor and then maintain activity to pickup more SOx in the next cycle through the regenerator. The increased H_2S released in the reactor effluent results in a 3-8% increase in total H_2S which can be handled in the existing gas concentration plant.

The common interpretation of Super DESOX® catalytic SOx control is shown below as a three step process [3], [5]:

1. **Step 1 - Sulfur Pickup – Oxidation in the Regenerator**

$$Scoke + O_2 \rightarrow SO_2$$
$$2SO_2 + O_2 \rightarrow 2SO_3$$

2. **Step 2 - $2SO_3$ Reaction in the Regenerator**

$$SO_3 + MeO \rightarrow MeSO_4$$

3. **Step 3 – Reduction Decomposition in Reactor and Stripper**

$$MeSO_4 + 4H_2 \rightarrow MeO + H_2S + 3H_2O$$

$$MeSO_4 + 4H_2 \rightarrow MeS + 4H_2O$$
$$MeS + H_2O \rightarrow MeO + H_2S$$

In step 1, the sulfur in the coke is oxidized to SO_2 which further reacts with oxygen in the regenerator bed to form SO_3. The oxidation of the SO_2 to SO_3 is considered the critical step for the efficiency of the additive; this reaction is catalyzed for a metal active compound present in the additive. In step 2, the sulfur, in form of SO_3 reacts with another metal active compound of the additive to form a stable metal sulfate, which is reduced in step 3, in the reactor either directly to H_2S or to a metal sulfide which is subsequently converted to H_2S by steam in the reactor or striper.

In October 22 the FCC unit started with the addition of the Super DESOX® additive. GRACE recommended an addition rate of the additive at 8% of the fresh catalyst addition, which was 2.8 ton/d, which means 224 Kg/d. At the same time GRACE recommended a base loading of three times 8% during four days (672 Kg/d).

Figure 9. Effect of the Super DESOX® Additive in the SOx emissions

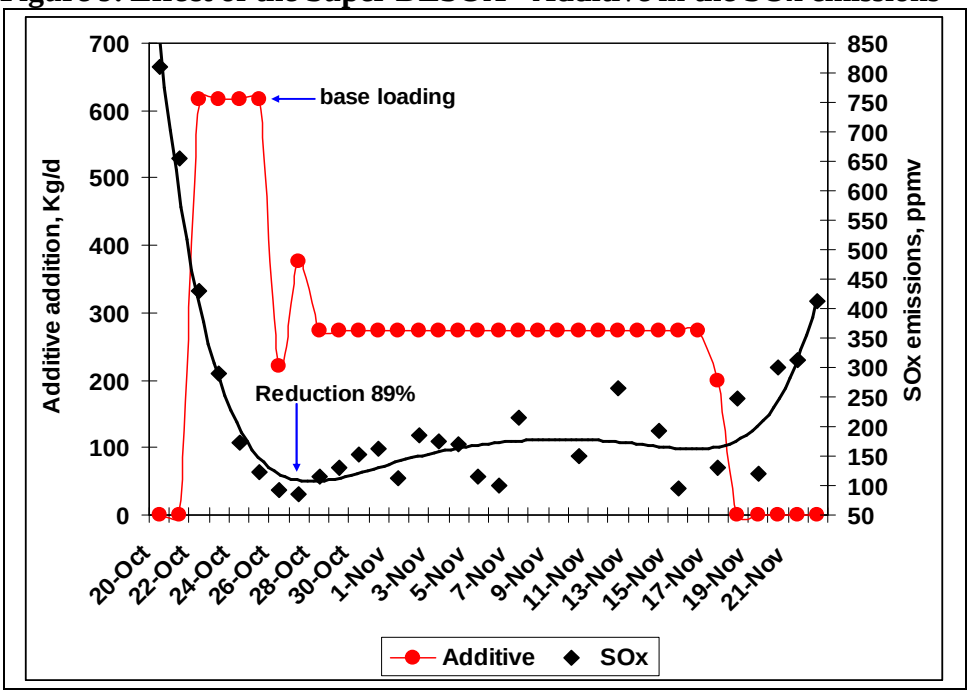


Figure 9, shows the different events during the Super DESOX® addition. During October 22-25, the addition was of 617 Kg/d, which corresponded to 9.2% less than the recommended amount for the base loading. It is interesting to see that the additive works immediately. In October 27 the refinery added 12% of the fresh catalysts addition, in order to compensate the total amount of the base loading; the reduction of the SOx emissions reached the maximum during this portion of the trial.

During October 30-November 17 the fresh catalyst additions rate increased to 3.5 ton/d with the addition of 1 ton/d of ECAT, due to the catalyst loss of 5 ton/d in the regenerator. This change decreased the additions of the additive to 6% and for that reason the SOx emissions start to increase. The addition of the additive finished on November 18 and the emissions started to increase at very high rate due to the catalyst and additive losses.

Figure 10. Effect of the Super DESOX® in the SOx emissions

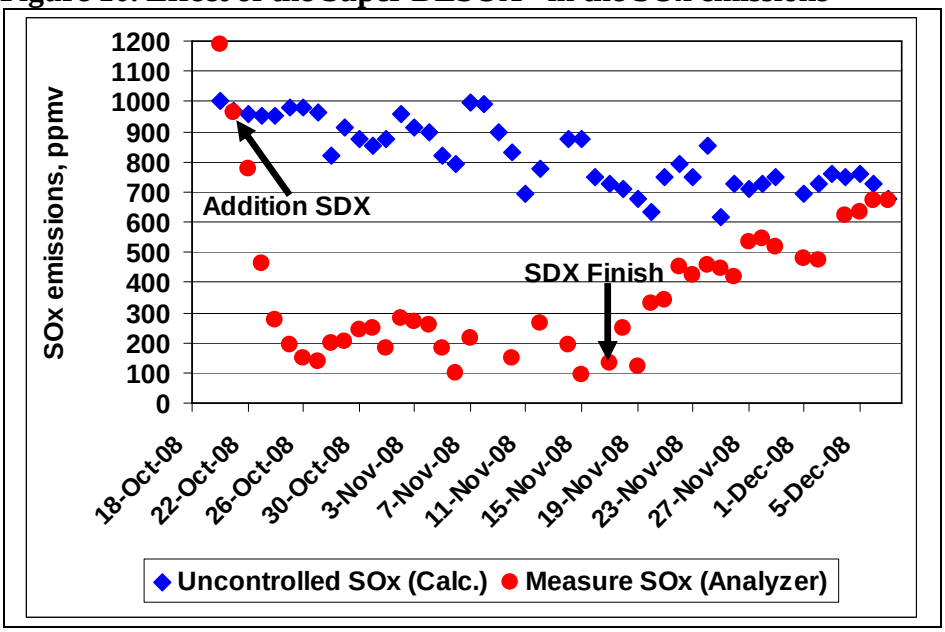
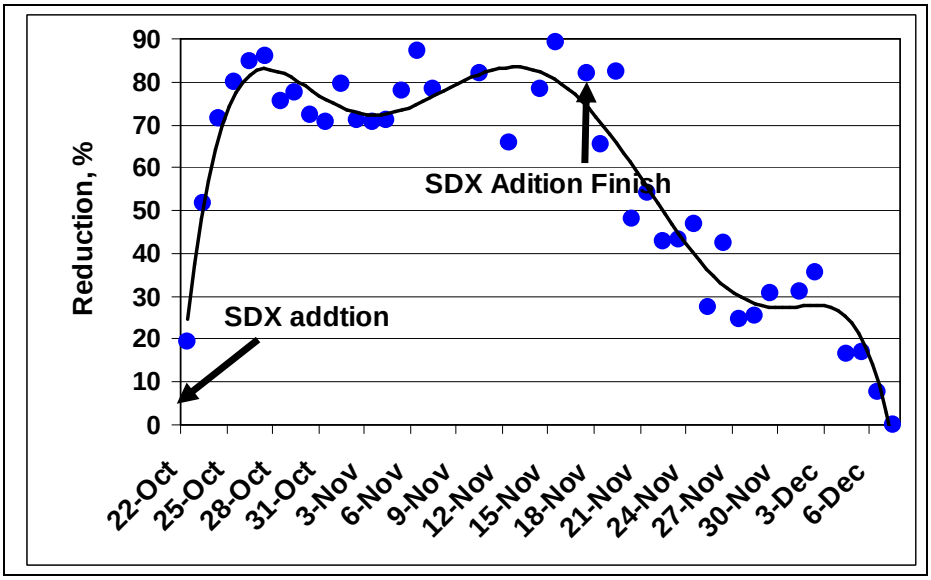


Figure 10 shows the reduction of the SOx emissions in presence of the Super DESOX® additive, along with the calculated "uncontrolled" SOx emission during the additive usage period, using equations 4 and 5. With normal operating conditions and with very good levels of excess of O_2 in the flue gas (higher than 2.0% vol), the emissions were reduced to an average of 150 ppmv SOx. If we consider that when the addition of the Super DESOX® started, the emissions were around 1000 ppmv (Figure 10), the SOx emissions were reduced by 85%.

Figure 11 shows that during the Super DESOX® addition the reduction of the SOx emissions were between 70-90% and during several days the reduction was 80-90%, even though during October and November 2008 the unit was losing catalyst and during November 2008 the addition of Super DESOX® was 7.8% of the fresh catalyst addition rate, instead of 8% as was recommended for the 2008 commercial trial.

Figure 11. Reduction of the SOx emissions – Trial 2008

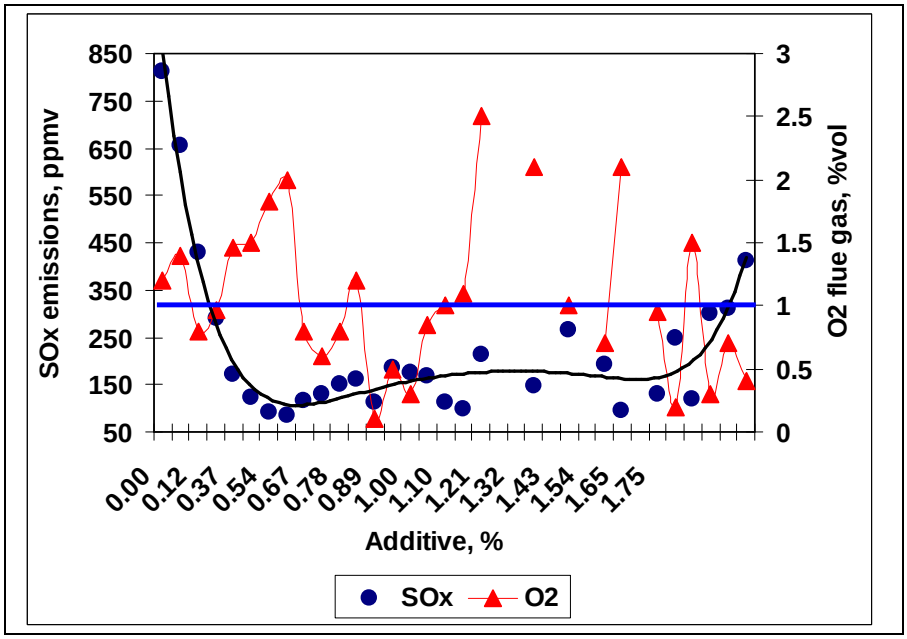


Thus, the objective of the trial, which was to reduce the SOx emissions by a level of 85%, was achieved. The addition of the Super DESOX® finished on 17-NOV-2008, and the results of figures 10 and 11 show that the additive still continued providing good activity, even though the catalyst loses were relatively high, and the fresh catalyst addition rate was increased to 4 Ton/day from November 18. The results of figures 10 and 11 show that on December 7 the unit reached the typical SOx emissions, for sulfur content in the feed of 1.0-1.2%wt.

It is known in the literature that one of the most important variables in the reaction to convert SO_2 to SO_3 in presence of the Super DESOX® additive is the concentration of the O_2 in the flue gas [5]. For this reason this type of additive works much better in total combustion units, where the O_2 concentration is high.

Figure 12 permits one to conclude that the lowest SOx concentration in presence of the Super DESOX® additive is reached with the higher O_2 concentration. Values of O_2 higher than 1% produce the lowest SOx emissions. In this plot, if the O_2 in the flue gas decreases, the SOx emissions increase.

Figure 12. O_2 effect in the SOx emissions with the Super DESOX®



4. Conclusions and recommendations

4.1 During the month of August and September several runs were conducted at the one FCC unit in the Caribbean. The results obtained during these runs permitted an understanding of the effect of the feed composition and operating conditions on the SOx emissions.

4.2 The complete characterization of the different feed components and the combined feed, as characterized by GRACE, permits us to conclude that the less crackable feed is the furfural extract, due to its lower API, higher sulfur, higher Conradson carbon, and Refractive Index. These properties are related with the higher aromatics content.

4.3 The MHC process, removes 90% of the sulfur, 80% of the concarbon, 95% of the vanadium and 100% of the nickel. At the same time the hydrogen content increases 6%, which is related with the 7.8% increase in the amount of saturates, which improved the yields of gasoline and LPG at the FCC unit and reduces the effect of the feed in the heat balance.

4.4 The feed components with the highest contributions to the SO_x emissions are the furfural extracts and the Flash distillates, which are sent to the MHC unit. The operation of the MHC is another condition that does affect the SO_x emissions.

4.5 In the normal FCC unit operating conditions and with the typical feed composition, the feed sulfur content is between 1.0-1.3 %wt. Under these conditions the total SO_x emissions were found to be between 600-850 ppmv. If the feed sulfur values are between 1.3-1.6 %wt, especially when the MHC unit is a low severity, the total SOx emissions increases to values between 850-1100 ppm. Finally, if the sulfur in the feed is higher than 1.6%wt, especially when the MHC unit is shut down, the SOx emissions increases to a values higher than 1100 ppm.

4.6 In the normal operating conditions and with a Super DESOX® concentration over 8% of the fresh catalyst additions rate it was possible to reduce 85-90% of the SOx emissions. When the unit started losing catalyst and the Super DESOX® additions decrease to 6-7% of the fresh catalyst additions rate, the reduction was between 70-80%.

4.7 To achieve the maximum SOx emissions reduction in presence of the correct amount of the Super DESOX®, is very important that the excess of O_2 in the flue gas concentration is over 1.0%.

4.8 The results obtained during the runs permitted GRACE to develop valuable correlations that the refinery can use to predict sulfur in the coke and SO_x emissions. Theses correlations are valuable tools for the refinery to calculate these operating conditions using normal and typical data.

5. Bibliography

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