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Successful ULSD Production at Petrobras' REFAP and RNEST Refineries with Innovative HDT Technology

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Abstract

This paper presents a real case story about the configuration and start-up of new Ultra Low Sulfur Diesel (ULSD) Hydrotreating units located at Petrobras' REFAP and RNEST refineries. These units design were based on a mixed virgin and cracked distillate feedstocks derived from Brazilian crudes that are typically naphthenic type with low sulfur and high nitrogen contents, high density and low cetane number in its Diesel range streams. These feedstocks features are quite particular in relation to the typical feed properties around the world.

The units configuration brings an innovative approach with aromatics hydrogenation step after a very deep desulfurization section, whose goal is not only to cope with the Diesel specification according to the most restrictive Brazilian fuel regulation (10 ppm maximum sulfur content, 0.850 maximum density and 48 minimum cetane number) but also bringing additional value to the refinery by keeping the Diesel volume swell during all cycle length with no reduction in the density gain at high WABT.

As expected, the innovative Diesel HDT technology is indeed leading to very good industrial results with ULSD production and improving product volume gain, consequently enhancing the refineries profit.

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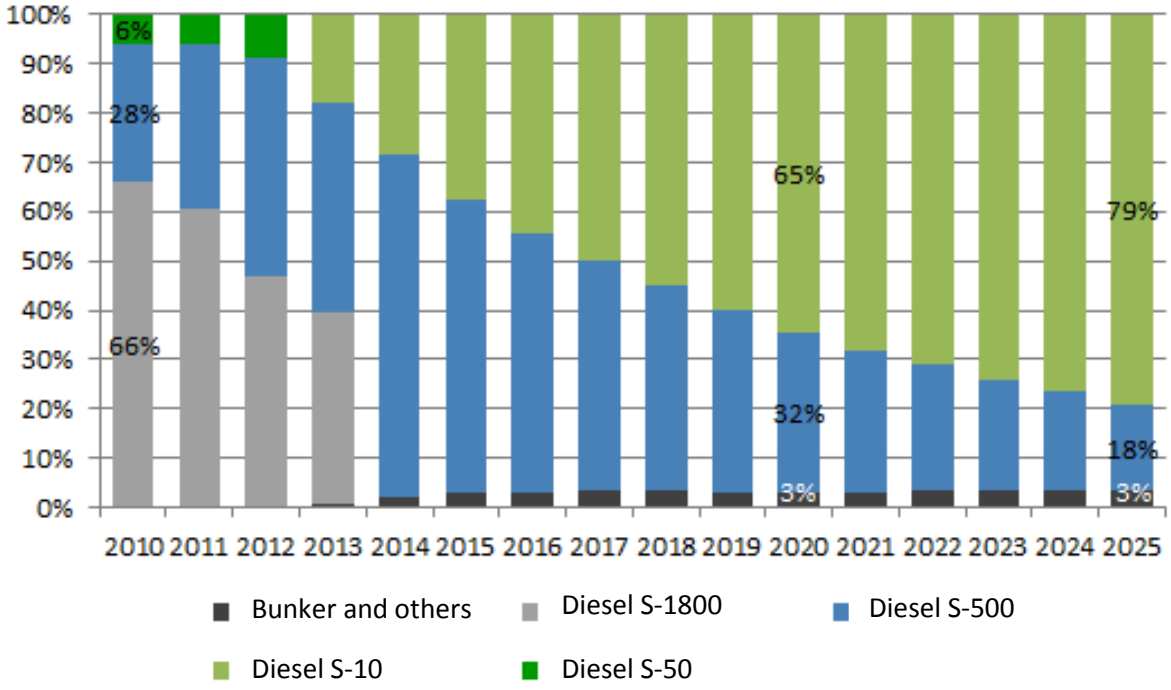
1. Introduction

Brazil oil refining domestic demand will grow from around 2,200 kbpd in 2015 to around 3,200 kbpd in 2020, and specifically Diesel will represent around 42% of the fuels market in the country by the end of this decade. In parallel, more and more restrictive environmental regulations are being applied, which consolidate the challenging scenario where this work is inserted.

Nowadays, there are only two diesel types in Brazil. Their commercial names are Diesel S500 and S10. Diesel S10 first begun to be commercialized in January 2013 and a quick pace expansion is expected. The graph below summarizes Brazilian Diesel sales divided into its different qualities from 2010 to a forecast for the forthcoming years.

Figure 1 - Diesel Distribution amongst Different Qualities in Brazil



Regarding specifications, the table 1 below shows the specification of these fuels.

Table 1 - Brazilian Diesel Fuels Specification

Properties	S500	S10
Flash Point (°C), min.	38	38
ASTM D86 (°C) – 10 v%	-	≥ 180
ASTM D86 (°C) – 50 v%	≤ 310	≤ 295
ASTM D86 (°C) – 85 v%	≤ 360	-
ASTM D86 (°C) – 90 v%	-	-
ASTM D86 (°C) – 95 v%	-	≤ 370
Density 20/4 °C	0.820-0.865	0.820-0.850
Viscosity @ 40 °C mm^2/s	2.0 - 5.0	2.0 - 4.5
Cetane Number, min.	42	48
PNA (wt%), max.	-	11
Sulphur (wtppm), max.	500	10

In order to cope with the presented situation, new refineries and new hydroprocessing projects have been materialized, in a tentative to avoid expensive fuel imports in Brazil. There have been several projects as part of this refining modernization trend focused on meeting these objectives. Through this paper it will be shown two of the hydroprocessing projects that have been successfully implemented in the southern and northeast regions of Brazil. They are units U-710 at Alberto Pasqualini Refinery (REFAP), Canoas, Rio Grande do Sul and U-31 at Abreu e Lima Refinery (RNEST), Ipojuca, Pernambuco, respectively.

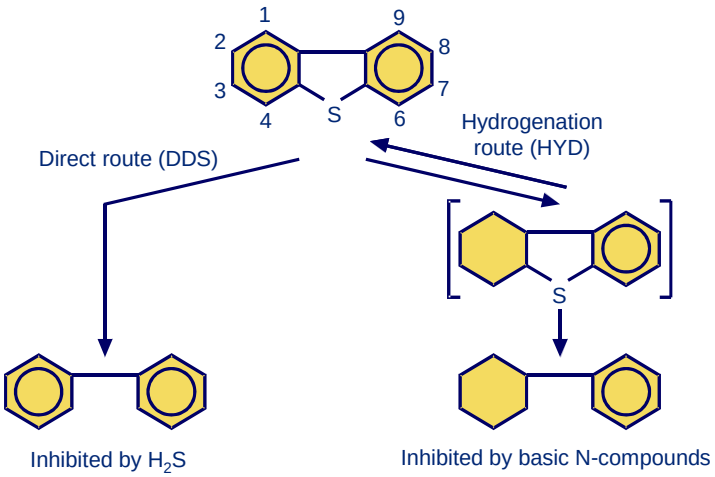
2 Main Issues in ULSD Production

2.1 HDS and HDN Activity of the Catalysts to Produce ULSD (< 10 ppm S)

As the primary process objective of the units would be to meet the < 10 ppm sulphur specification, in a cycle of minimum 3 years, a fundamental understanding of HDS (hydrodesulphurization) reaction pathways and catalyst functionality is essential.

At the high degree of desulphurization for which the unit should be designed, essentially all the sulphur species would be converted in the first 30-40% of the total catalyst volume. Only the most difficult to remove sulphur compounds remain after this point, and therefore become reaction rate limiting for HDS. Feed boiling range, feed type and sulphur speciation by sulphur specific gas chromatography provide information to quantify the amount of sterically hindered dibenzothiophenes (DBT) in the feed and therefore a basis for establishing the required operating conditions.

Figure 2 - Diesel Hydrodesulphurization Routes



A very high concentration of basic nitrogen was measured in the design feed. Basic nitrogen strongly inhibits the catalysts hydrogenation function by occupying acidic sites, with the consequence that fast reaction rate desulphurization by the hydrogenation route (HYD) becomes very limited.

However, a catalyst with high HDN (hydrodenitorgenation) activity operated under feasible processing conditions, e.g. high H_2 partial pressure, can reduce the concentration of inhibiting basic nitrogen in the reactor to a level where the hydrogenation routes are not only utilized but also becomes the dominant reaction route. A state of the art NiMo type catalyst is the preferred catalyst for such scenario; offering the highest HDN activity for removing basic nitrogen and maximum hydrogenation activity, to ensure a high level of density reduction and cetane uplift through aromatic saturation.

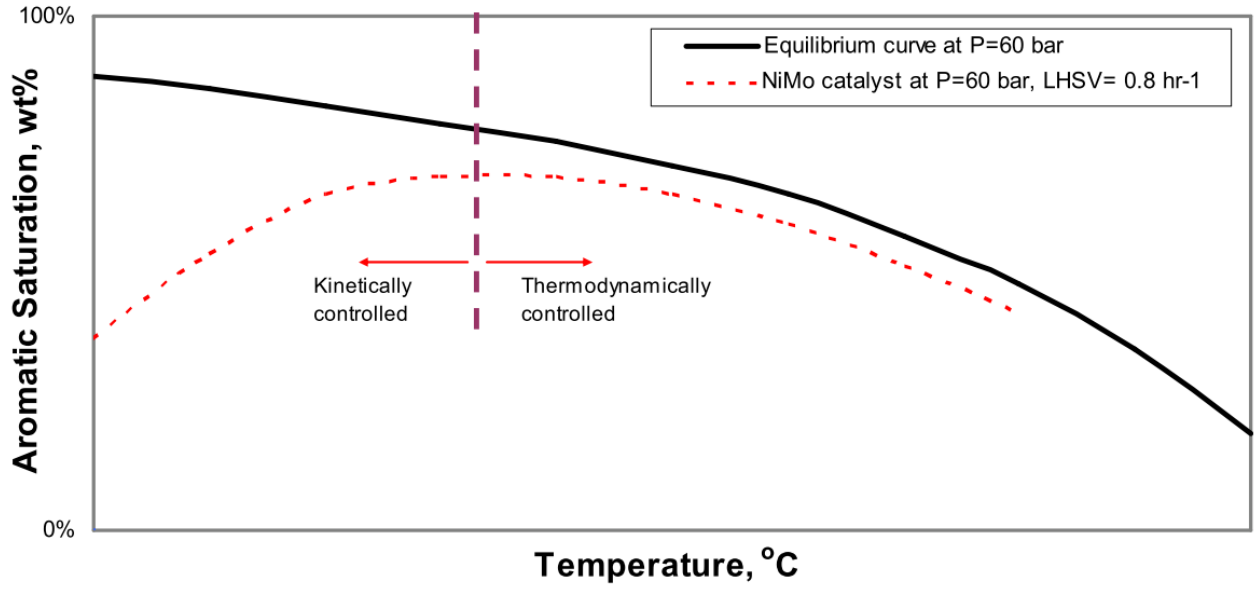
2.2 Density Reduction, Cetane Improvement, HDA and H_2 Consumption

Considering the relatively low sulphur content in the design feed, other process objectives such as cetane uplift becomes limiting / design giving. The premise for cetane uplift, as well as density reduction is HDA (aromatics hydrogenation); not only cascading of polyaromatic species down to lower molecular weight monoaromatics, but saturation of monoaromatics into cyclic saturates.

Aromatic saturation is not limited by thermodynamic equilibrium at typical start of run conditions; however, it can be limited at typical end of run conditions, when the end of run temperature approaches. The reactor outlet temperature is determined by the required WABT for desulphurization, the overall temperature rise and the quench added between beds to control the overall temperature rise. Increasing the number of catalyst beds in the unit with inter-bed quench lowers the reactor outlet temperature for a given WABT and reduces the thermodynamic limitation at end of run or extends the run length by raising the WABT at a given outlet temperature. This was a key aspect to define the number of beds in each reactor.

The graphic below illustrates saturation of aromatics in the temperature operating window typical for a hydrotreater, where a low temperature can be used to avoid the thermodynamically limited constraints. At low operating hydrogen partial pressure the overall aromatic saturation percentage is low, and in particular at elevated temperatures (equilibrium constraint).

Figure 3 - HDA Kinetic and Thermodynamic Relationship at Constant Pressure



However, at higher hydrogen partial pressure a higher saturation percentage can be obtained and the equilibrium constraint diminishes as the optimum for aromatic saturation shifts further to the right. In other words, a greater part of the operating window becomes kinetically controlled.

The figure illustrates saturation numbers for a catalyst with SOR activity. At EOR temperatures the catalyst is deactivated and thus the true saturation percentage would in fact be lower than illustrated in the plot. It is very important to take this into consideration when selecting the proper operating conditions for a new unit design, otherwise the consequence could be a unit with insufficient aromatic saturation capabilities at EOR, and hence insufficient cetane uplift.

Using high quench gas rates helps lower reactor outlet temperature at constant average bed temperature. This reduces equilibrium limitations while maximizing the rate of aromatic saturation.

Higher catalyst activity or volume allows for lower operating temperatures and therefore more favourable conditions for aromatic saturation. Low operating temperatures also lowers the rate of catalyst deactivation and the time that the unit can operate before requiring catalyst replacement.

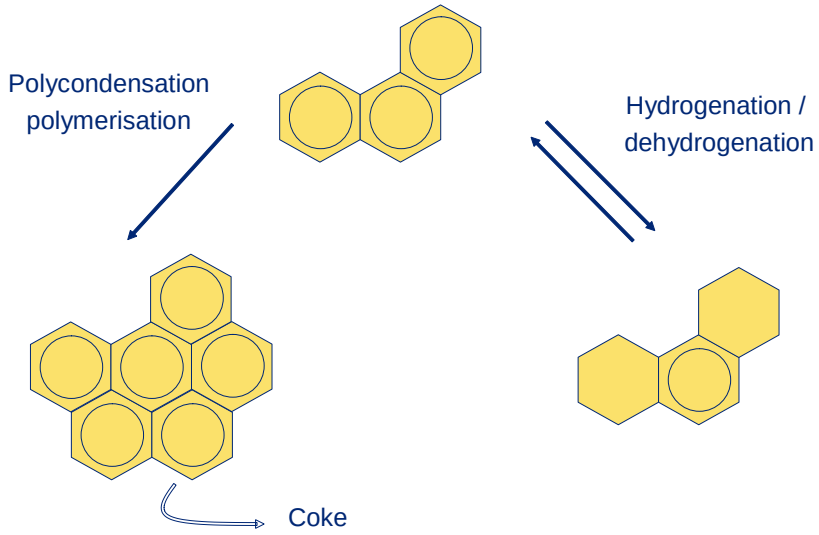
Treat gas rate also has an effect on both the rate of aromatic saturation and the equilibrium constraint. Since hydrogen is consumed through heteroatom (sulphur and nitrogen) removal and aromatic saturation, the hydrogen partial pressure decreases with the extent of reaction through the reactor. Higher hydrogen treat gas rates (excess hydrogen) reduce the drop in hydrogen partial pressure through the reactor. The rate and the maximum extent of aromatic saturation are direct functions of hydrogen partial pressure.

2.3 Catalyst Deactivation Rate

Modern pilot plant units ensure high repeatability and accuracy in testing, while substantially reducing artificial deactivation. In combination with comprehensive deactivation models, incorporating a wide range of feed factors and the actual operating conditions, catalyst deactivation in large scale units can be accurately predicted. Once the appropriate operating conditions for meeting all product specifications SOR through EOR have been established, an iteration process takes place where unit design variables are adjusted until the desired cycle length is achieved. For every change in variable during the iteration process, a new deactivation rate is determined and the cycle length is adjusted accordingly.

A high content of polyaromatic species in the feed blend increases the potential for polycondensation and thus coke formation on the catalyst. Hence, when processing coker gasoil and light cycle oil, the deactivation rate of the catalyst is typically higher compared to a straight-run only service. However, by carefully selecting the proper operating conditions, the polycondensation reaction can be kept at a minimum, and high percentages of cracked stock can be processed without accelerated deactivation of the catalyst as a result.

Figure 4 – Polycondensation Mechanism Leading to Coke and Catalyst Deactivation



3. ULSD Production Technology

3.1 Process Configuration

Diesel hydrotreating technologies have been operating in many refineries for over 50 years. Although the core basic design of hydrotreaters could be initially considered standard, since the introduction of Ultra-Low Sulphur Diesel (ULSD) in the last years with higher severity requirements, most of the hydrotreating patterns, schemes and technologies such as the reactor internals, catalysts and also capital and operating costs have been evolving and changing significantly. The severity required to produce ULSD has been changing and therefore the cost of new unit designs.

New crude oils available in the market such as Brazilian crudes with high aromatics content and high nitrogen require a better understanding of the conditions to customize the production of ULSD. Nitrogen contents were somewhat higher than typical streams and for this case the heavy virgin gas oil was much heavier than typical processed in a diesel HDT unit. Although it seemed to be possible to achieve the low sulphur objective, it initially appeared challenging to reduce the aromatic content and the density of the product, while considering the achievement of minimum 3 years cycle length.

The main objective of the units design was to obtain diesel with less than 10 ppm sulphur while achieving a significant increase in cetane number together with a minimum reduction of 0.03 in diesel density (20/4 ºC) or S.G. from mixed virgin and cracked distillate feed derived from Brazilian crude.

3.2 The Polyshift Technology

In order to achieve the necessary aromatics conversion along the whole cycle, the key concept introduced with is a third Polyshift reactor. It is composed by one bed of NiMo catalyst and has the objective to lower the product density further by saturating polyaromatics to monoaromatics at low temperatures. The hydrotreating reactor effluent is cooled by exchange with incoming feed before it enters the final Polyshift reactor. The aromatic reaction is an equilibrium reaction and is favoured by the lower temperature at this reactor.

Under the operating conditions of the studied units, up to 30% of the monoaromatic compounds present will be hydrogenated in the HDS and Polyshift reactors, while most of the polyaromatic compounds present are partially hydrogenated to form monoaromatics at SOR. At higher temperatures (EOR) or at lower hydrogen partial pressure, the rate of the reverse dehydrogenation reaction increases relative to the hydrogenation reaction due to equilibrium constraints, and hence the amount of di and triaromatics in the reactors effluent from the HDS reactors is higher than at SOR. However, by treating the HDS reactor effluent high in polyaromatics at lower temperature in the Polyshift reactor, the hydrogenation reaction is favoured and more polyaromatics are saturated as a result. Hence, with this unit configuration, the optimum HDA activity can be met at both SOR and EOR, and even at a relatively low pressure and thus low operating costs and low CAPEX, while achieving the desire ULSD specification over a cycle length of minimum 3 years.

3.3 Reactor Internals

Reactors internals technology has been significantly evolving in the last decade. Although this technology might have not been critical for traditional hydrotreating, it is indeed critical for ULSD production. This technology is important to mainly improve the distribution and mixing of liquid and gas across the entire reactor cross sectional area.

New advanced reactor internals can reduce catalyst volume, reduce reactor design sizes, reduce time for catalyst replacements and also improve unit reliability. They can reduce radial temperature spreads in catalyst beds, allowing higher WABT at EOR and hence longer time. Also, can reduce hot spot temperature with reduced risk for coke formation and temperature excursions and improve unit reliability.

The most modern reactor internals technologies have some patented components:

- Vapor Lift Distribution Tray (VLT) design features a closely spaced array of nozzles designed to disperse the liquid and gas evenly across the top of the catalyst bed. The nozzles operate on a vapour assist principle, by, which the vapour flows through the inlet apertures/slots on the nozzle and thereby lifts the liquid through the nozzles and disperses it into the catalyst bed;

- Compact Vortex Mixer with a vortex type mixing chamber receives the gas and oil equally from all quadrants of the quench collection tray through slide–nozzles. There the fluids reach the dispersed flow regime forcing the mixed media into a centrifugally path where the mixed gas and oil interchanges with each other until it reaches the orifice of the mixer, where the mixed liquid and vapour are reaccelerated, reaching the disperse flow regime, again ensuring that the mixture is mixed sufficiently to reach an equilibrium before it is re-distributed onto the next catalyst bed.

4. Petrobras' Units Implementation

4.1 Pilot Plant Study

A pilot plant test is the preferred method to accurately determine feedstock reactivity and thus the required operating conditions to produce a ULSD product with several stringent specifications. In consequence, a pilot unit studies were commissioned to confirm the ability of the selected process configuration to produce

10 ppm sulphur diesel, while meeting the required cetane uplift and density reduction, SOR through EOR. Pilot plant testing also provided the basis for the units design.

4.2 Unit U-710

The unit was designed by HTAS and started-up on September 2014. This unit is located at Petrobras' Alberto Pasqualini Refinery - REFAP (Canoas/Rio Grande do Sul/Brazil). It is composed by three reactors, two of them with two beds each and NiMo Catalysts, and the third polyshift reactor with a single bed. All of them use NiMo catalysts. These were used in pilot plant to obtain the basic design data aiming less than 10 ppm sulphur while achieving a 7.5 numbers increase in cetane number together with a minimum reduction of 0.03 in diesel density (20/4 ºC) or S.G. from a blend of approximate 60 wt% heavy straight-run gas oil (HSRGO), 10 wt% of coker gas oil (CGO) and 30 wt% of FCC light cycle oil (LCO) derived from Brazilian crude slate. The project has considered 6,000 m³/d of capacity processed in three reactors in series, space velocity of 0.57 h^{-1} and 84 kgf/cm² inlet first reactor pressure.

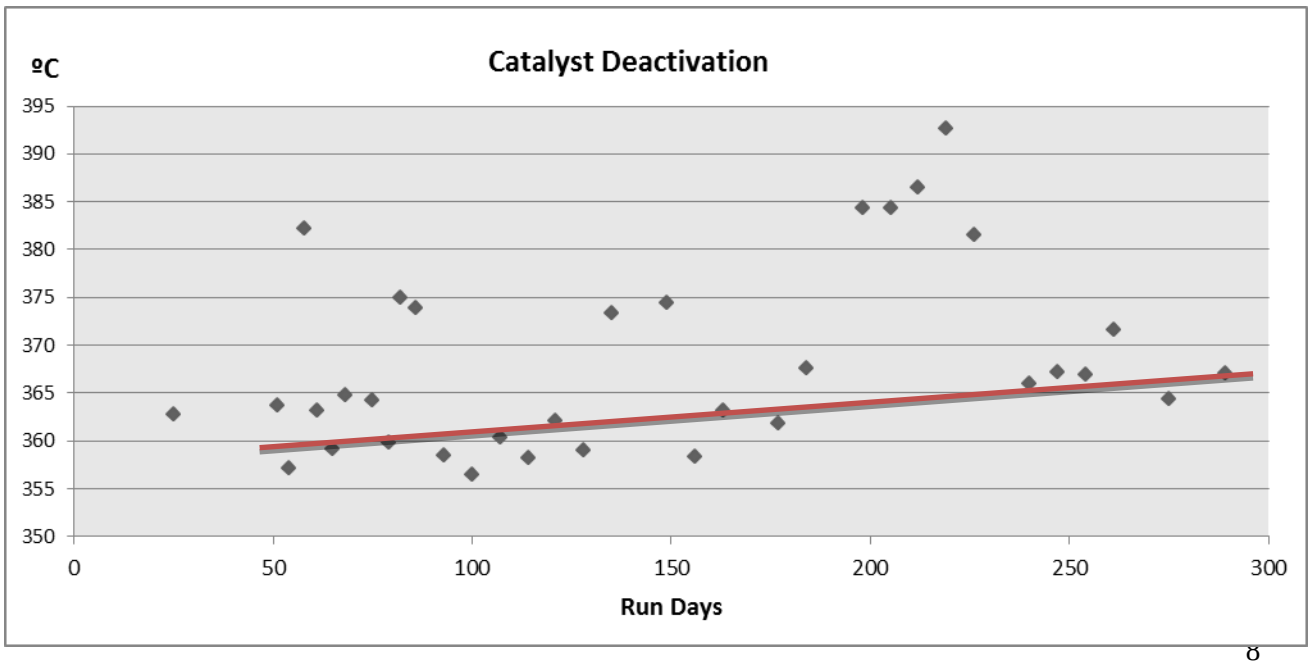
The table 2 shows the typical Diesel S10 production in this unit:

Table 2 – Unit U 710's Industrial Diesel S10 Production

Date	May 2015	
Properties	**Feedstock**	**Product**
Density @ 20/4 ºC	0.8605	0.8410
Sulphur (wtppm)	2,130	3.2
Nitrogen (wtppm)	925	1.1
Cetane Index ATM D4737	41	46
Distillation ASTM D86 (ºC) 10 v% - 50 v% - 90% - 95 %v	210/256/332/362	208/2251/330/360
Operation Conditions Feedstock Rate (m³/d) Feedstock Composition (vol%) Reactor Inlet Pressure (kgf/cm²) WABT (ºC) Hydrogen Consumption (kNm³/h)	6,000 SRD 56% + KGO 19% + Kerosene 2,5% + LCO 22.5% 84 354 37.1	

The HDS deactivation rate is shown in the graphic below:

Figure 5 – Deactivation Rate for REFAP U-710 in the First 300 Run Days



4.3 Unit -31

The unit was designed by HTAS and started-up on March 2015. This unit is located at Petrobras' Abreu e Lima refinery - Rnest (Ipojuca/Pernambuco/Brazil). Because of its size, the unit comprises two twin lines. Each of them has three reactors, of which the first two have two beds and the third polyshift reactor is a single bed one. All of them have NiMo catalysts. These were used in pilot plant to obtain the basic design data aiming less than 10 ppm sulphur while achieving a 8.0 numbers increase in cetane number together with a minimum reduction of 0.035 in diesel density (20/4 ºC) or S.G. from a blend of approximate 63 wt% heavy straight-run gas oil (HSRGO) and 37 wt% of coker gas oil (CGO) from Marlim Brazilian crude. The project has considered 13,000 m^3/d of capacity processed in two trains with three reactors in series each, space velocity of 0.56 h^{-1} and 124 kgf/cm^2 inlet first reactor pressure.

The table 3 shows the typical Diesel S10 production in this unit:

Table 3 – Unit U-31's Industrial Diesel S10 Production

Date	**Jun 2015**	
Properties	**Feedstock**	**Product**
Density @ 20/4 ºC	0.8443	0.8312
Sulphur (wtppm)	1243	1.5
Nitrogen (wtppm)	252	1.9
Cetane Index ATM D4737	51	55
Distillation ASTM D86 (ºC) 10 v% - 50 v% - 95 %v	216/286/375	213/279/368
Operation Conditions Feedstock Rate (m^3/d) Feedstock Composition (vol%) Reactor Inlet Pressure (kgf/cm^2) WABT (ºC) Hydrogen Consumption (kNm^3/h)	 7,890 SRD 63% + CGO 37% 96 324 31	

5. Conclusion

Analyzing the real data from the studied units it can be concluded that the objectives persecuted by the implemented technology of the unit are being reached. Both units are being able to produce specified S10 Diesel whenever required. Also, the unit U-710/REFAP shows a value of around 0.9ºC/month of deactivation, which fits very well with its design. The unit U-31/RNEST has been running for few months only and therefore it is not possible to get proper conclusions on catalyst deactivation.

Regarding Diesel swell, volume increase is significantly in both units. In U-31/RNEST, the unit is still not running in steady state conditions but it can already be seen a volume swell in the Diesel stream of 2.0%. The unit U-710/REFAP, which has been running for more than 300 days, shows a typical volume increase of 2.7%.

Both numbers have important impact on the refineries profit, showing that the technology is a successful choice not only to meet the highest diesel specs but also to bring value to the unit.

6. Bibliography

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