REPSOLYPF STRATEGY FOR PRODUCTION OF CLEAN FUELS

Fernando Albertos de Benito, Luis Casado Padilla*
Repsol YPF – Dirección de Tecnología – Móstoles, Madrid, España
***Repsol YPF – Dirección de Planificación y Control - Madrid, España**

RepsolYPF is an integrated oil and gas Company that operates all over the world. Our refining installed capacity is 1.1 MM bpd. 70% of this capacity is installed in Spain and the rest in several South American countries, mainly in Argentina. Most of our fuels produced in our five Spanish refineries are sold in local markets and hence they have to fulfil with the stringent European legislation. This paper shows the strategy followed by RepsolYPF during the last few years to adapt its refining structure in Spain to the production of clean fuels, and particularly to the production of ultra low sulphur diesel (< 10 wppm S). RepsolYPF is already producing 10 ppm sulphur gasoline and diesel oil for the Spanish market, as well as the regulated quality (50 ppm sulphur).

As a starting point for this paper we take the situation in the year 2000: a new specification for diesel had just come into operation that limited sulphur in diesel to 350 ppm and all refineries had been adapted for this new spec. At this time an internal work programme was launched covering the following steps:

1- HDS industrial Units assessment, with the main objective of defining the real Units and refineries capacity to produce diesel with 50 ppm sulphur. The assessment included a detailed kinetic and process study carried out internally for all refineries, consultations to catalyst manufacturers and licensors and performance of test runs to a number of industrial Units. It was concluded that, considering the projects that were already in progress (one new HC and two new MHC units), four out of the five refineries would be all right for producing 50 ppms fuels. In the remaining refinery some shortage of HDS capacity was foreseen. At that stage it was decided that the additional HDS capacity to be installed should allow this refinery to produce 100% of its diesel auto with 10 ppm of Sulphur. After a technology selection process a new 24 kbpsd Unit was approved.

2- In parallel to 1) our Technology Division was asked to develop and provide the necessary tools for carrying out the internal studies required to adapt the refineries to the production of clean fuels. Through an extensive programme of pilot plant testing and analysis of industrial data, the following items have been obtained:
- Kinetic models for ULSD production
- Deactivation models for industrial HDS unit operation
- Industrial Unit follow up model
- Classification of commercial catalysts performance
- General HDS unit simulation model

3- On view of the specs evolution (10 ppm fuels to be introduced gradually) a new assessment was launched to define the refineries capacity to produce simultaneously 50 and 10 ppm.

4- Finally, engineering studies were carried out for all the industrial units. These studies were the basis for definition of required revamps to adapt 100% of the production to the 10 ppm scenario. To carry out these studies, tools developed within 2) have been widely used, together with consultations to catalyst manufacturers and licensors.

In this paper we describe the activities outlined above, with special attention to the industrial Units performance in the production of diesel with 50 and 10 ppm sulphur.

1.- Introduction

RepsolYPF is an integrated oil and gas Company that operates all over the world. Our refining installed capacity is 1.1 MM bpd. 70% of this capacity is installed in Spain and the rest in several South American countries. Most of our fuels produced in our five Spanish refineries are marketed in Europe and hence they have to fulfil with the stringent European legislation. This paper shows the strategy followed by RepsolYPF during the last few years to adapt its refining structure in Spain to the production of clean fuels, and particularly to the production of ultra low sulphur diesel (< 10 wppm S).

As a starting point for this paper we take the situation in the year 2000: a new specification for diesel had just come into operation that limited sulphur in diesel to 350 ppm and all refineries had been adapted for this new spec. At this time an internal work programme was launched covering the following steps:

1- HDS industrial Units assessment, with the main objective of defining the real Units and refineries capacity to produce diesel with 50 ppm sulphur. The assessment included a detailed kinetic and process study carried out internally for all refineries, consultations to catalyst manufacturers and licensors and performance of test runs to a number of industrial Units. It was concluded that, considering the projects that were already in progress (one new HC and two new MHC units), four out of the five refineries would be prepared for producing 50 ppm fuels. In the remaining refinery some shortage of HDS capacity was foreseen. At that stage it was decided that the additional HDS capacity to be installed should allow this refinery to produce 100% of its diesel auto with 10 ppm of Sulphur. After a technology selection process a new 24 kbpsd Unit was approved.

2- In parallel to 1) our Technology Division was asked to develop and provide the necessary tools for carrying out the internal studies required to adapt the refineries to the production of clean fuels. After an extensive programme of pilot plant testing and analysis of industrial data, the following items were obtained:

- Kinetic models for ULSD production
- Deactivation models for industrial HDS unit operation
- Classification of commercial catalysts performance
- General HDS unit simulation model

3- On view of the specs evolution (10 ppm fuels to be introduced gradually) a new assessment was launched to define the refineries capacity to produce simultaneously 50 and 10 ppm.

4- Finally, engineering studies were carried out for all the industrial units. These studies were the basis for the definition of required revamps to adapt 100% of the production to the 10 ppm scenario. To carry out these studies, tools developed within 2) have been widely used, together with consultations to catalyst manufacturers and licensors.

In this paper, the activities outlined above are described.

2.- Fuels production in 2000

In 2000 RepsolYPF refineries in Spain were producing gasoline and diesel with 150 and 350 ppm sulphur respectively, according to the specifications that had just come into operation. Also, new projects, directed to increase the refineries capacity to produce fuels with lower sulphur concentrations had already been approved and were at different stages of implementation. The most significant projects were:

- High pressure HVGO hydrocracker for Tarragona refinery
- VGO/HCGO Mild Hydrocracker units for Puertollano and Coruña refineries
- FCC naphtha splitters for our FCC based refineries

These new Units would allow us to further improve the quality of our fuels, and also to increase our diesel production capacity, as required by market trends. The following table briefly shows our refineries production schemes for diesel fuel, considering the new Units already in operation:

Cartagena:	Hydro skimming Two HDS Units adapted for present specification 100% Diesel pool hydrotreated (except for heating oil)
Coruña:	Mild HC + FCC + Delayed cocker Two HDS Units adapted for present specification 100% Diesel pool hydrotreated (except for heating oil)
Petronor	VGO HDT + FCC + Visbreaker Three HDS Units adapted for present specification 100% Diesel pool hydrotreated (except for heating oil)
Puertollano	MHC + FCC + Delayed coker Five HDS Units adapted for present specification 100% Diesel pool hydrotreated (except for heating oil)
Tarragona	ISOMAX + HVGO HC Three HDS Units adapted for present specification 100% Diesel pool hydrotreated (except for heating oil)

The table shows the basic diesel production schemes. Of course, important flexibilities were in place, and the previous table cannot be considered as a fix picture of our refineries.

At that time, three scenarios were considered for study:

- Capabilities for 100% fuels production complying with the 50 ppm sulphur spec

- Define refineries capacity to produce simultaneously fuels complying with the 50 and 10 ppm maximum sulphur spec with

- Define refining schemes, revamps and new projects for adapting 100% of our fuels production to the 10 ppm sulphur spec.

To carry out this job a working group was formed headed by the Strategic Planning Department, and including people from our Technical and Engineering Divisions, R&D and refineries. After a first analysis of the assignment and capabilities, it was decided that the study could be fully developed internally by RepsolYPF, with precise external consultations where required. For the third scenario, projects definition up to a conceptual engineering stage would be done internally.

It was clear to us that kinetic and simulation tools valid for the 10 and 50 ppm scenarios would be required to perform the studies. At that time, our Technology Division was already working on these developments, and they were asked to accelerate the pace to have the tools available.

Next paragraph resumes the work carried out by our Technology Division to develop the required kinetic and simulation tools. Then in 4, the outcome of the scenarios study is also resumed.

3.- R&D Developments

A complete HDS simulation tool has been developed, that integrates kinetic, deactivation, catalyst ranking and thermodynamic models. Pilot plant and industrial data have been used for the developments and calibrations. The models have proved to reproduce the operation of industrial units making 50 and 10 ppm sulphur products. These tools have been employed in the analysis of scenarios shown in this paper

3.1.- Kinetic models for ULSD production

A large number of reactions take place during the hydrotreatment process. In many ways they are interrelated since they take place simultaneously on the same catalyst and are affected by the same operating variables. Also, a reactant for one reaction may act as an inhibitor for another and vice versa. To cover the whole picture, kinetic models have been developed to describe the main process that take place during hydrotreatment:

Hydrodesulphurisation (HDS)
Hydrodenitrification (HDN)
Hydrodearomatisation (HDA)
Olefin hydrogenation (HYD)
Hydrocracking (HC)

The experimental data used for deriving these models were obtained in a large number of pilot plant trials, carried out at our R&D facilities. Main parameters considered for the experimental design were:

1- Operating conditions

- Temperature: Isothermal temperature for pilot plant (WABT adiabatic reactor average temperature for Industrial reactor)
- Reactor total pressure: Total pressure for pilot plant (Reactor outlet pressure for industrial unit)
- Hydrogen purity: 100% for pilot plant (total hydrogen to reactor purity for industrial unit)
- Reactor partial pressure: calculated at reactor outlet
- H2/Hydrocarbon ratio: for industrial reactor, the total hydrogen to reactor is considered
- LHSV: hydrocarbon flow-rate/catalyst volume

2- Feed properties

- Total sulphur concentration
- Specific gravity
- Distillation curve (D-86, T10%, T95%)

- Type of feed (Straight run, conversion)
- Origin of crude oil (for SR feeds)

3- Type of catalyst

- NiMo, CoMo

The range of variation of these parameters during our pilot plant tests were selected to cover that of our industrial units. The following table shows such ranges:

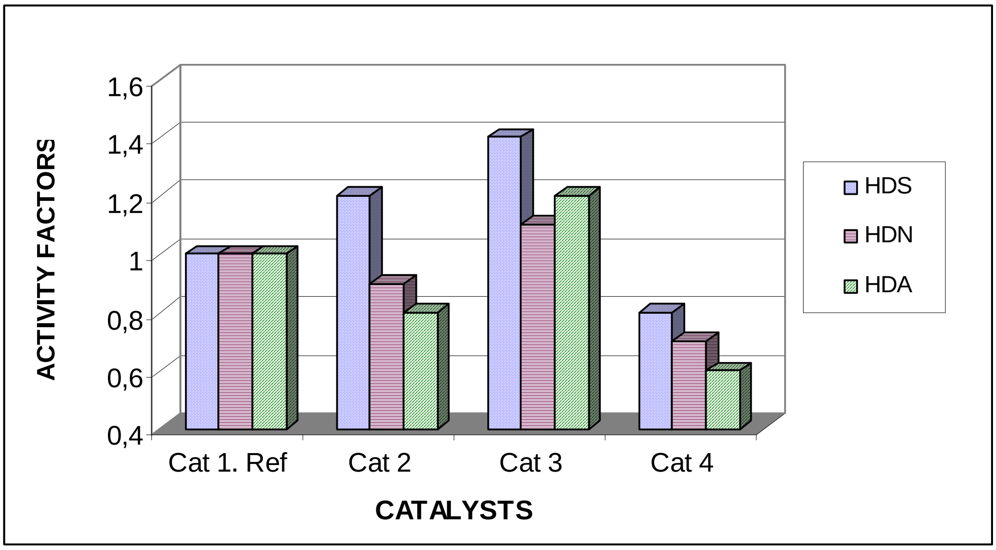
OPERATING VARIABLES	
WABT, ºC	280 -390
LHSV, h^{-1}	0.5 –1.5
Pressure, kg/cm^2	30-60
H_2 /HC, Nm^3/m^3	200-400
FEED PROPERTIES	
Type	LSR; HSR; LCO; LCGO
Origin of crude oil	West Africa; North Africa; Middle East; America
Sulphur, ppm	2500-16000
Nitrogen, ppm	100 –350
Density, g/cc	0.82 – 0.88
D86 10% ºC	220 –305
D86 90% ºC	280 – 365
CATALYST TYPE	
CoMo and NiMo, fresh and used (SOR and EOR)	

The kinetic models developed were mainly empirical, and so it is important that all industrial conditions, feed and product characteristics are well covered within the experimental range tested in pilot plant. Simultaneous parameters fitting was used to obtain kinetic parameters for all reactions involved. Following this procedure kinetic expressions for the processes involved were obtained (HDS, HDN, HDA, HDPA, HYD, and HC). As an example, the sulphur conversion would have the following dependences:

$X_S = f_1$ *(CAT) x* f_2 *(OP. CONDITIONS) x* f_3 *(FEED PROPERTIES) x* f_4 *(UNIT CAL.)*

f_1 *(CATALYST):* Function of catalyst employed. CoMo or NiMo, fresh or spent, implies modification of kinetic parameters. Within a given type, use of different materials (manufacturer, model) implies different activity factors. The following figure illustrates these effects:

Activity factors obtained from pilot plant results



Activity factors for most commercial catalyst have been obtained through pilot plant runs. The results of these runs are used for model development as well as for catalysts selection in commercial applications.

<u>*f_2 (OPERATING CONDITIONS):*</u> Takes into account the effect on conversion of the operating conditions employed. Particular functions were obtained for CoMo and NiMo catalyst reflecting differences in reaction pathways and reactivity.

We found much benefit in the accuracy of models prediction by using hydrogen partial pressure (P_{H2}) at reactor (or bed) outlet as a kinetic variable. It makes calculations more difficult since it is necessary to simultaneously understand and quantify all processes that affect this variable (hydrogen consumption by every reaction, changes in feed to product characteristics (D-86, ρ, etc), heat release, and vaporisation).

As an example, for sulphur conversion f_2 is dependent on:

$X_S \rightarrow f_2\ (T, LHSV, P_{H2}, P_{SH2})$

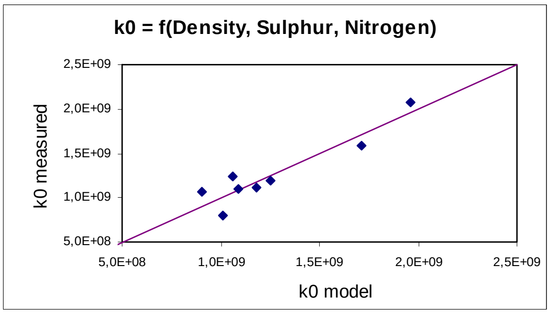
Some feed properties affecting PH2 calculation are:
Olefin content → Br No
Aromatic content → ρ, μ
Nitrogen content
Distillation curve

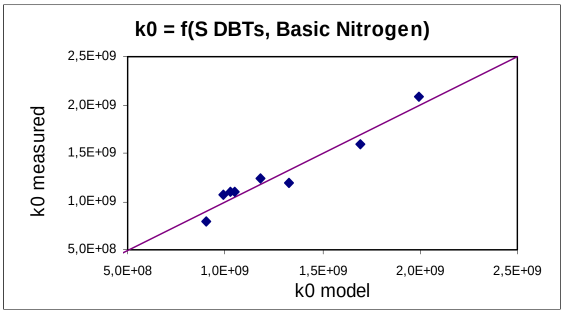
Consequently, feed properties that may not be directly included as feed kinetic parameters (see below), have an effect on the reactor performance, and hence on the output of our kinetic models.

<u>*f_3 (FEED PROPERTIES)*</u>

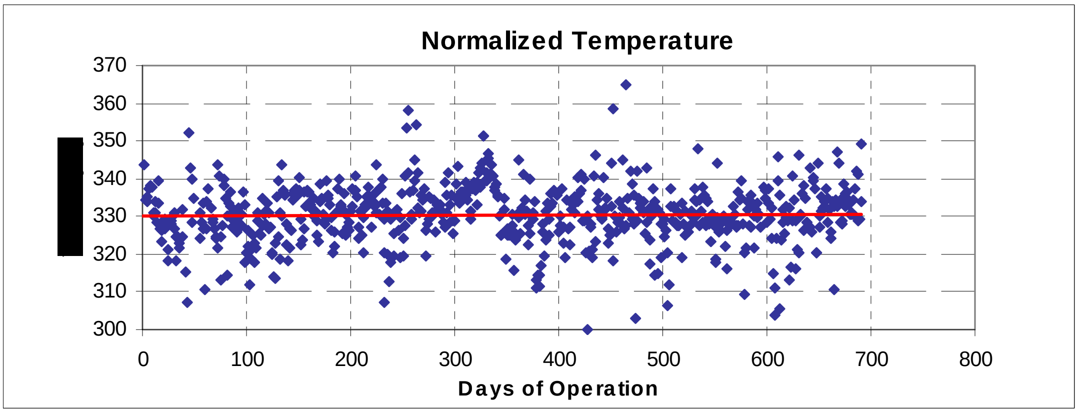
We found that a key factor to improve the prediction capacity of our models was to include a function of feed properties that reflected differences in feed reactivity towards the reaction considered. Of course, more rigorous models do not need to include such functions, since they are based on mechanistic reaction path-ways, inhibiting effects etc. However for us it has been of great help to consider and quantify these feed dependences.

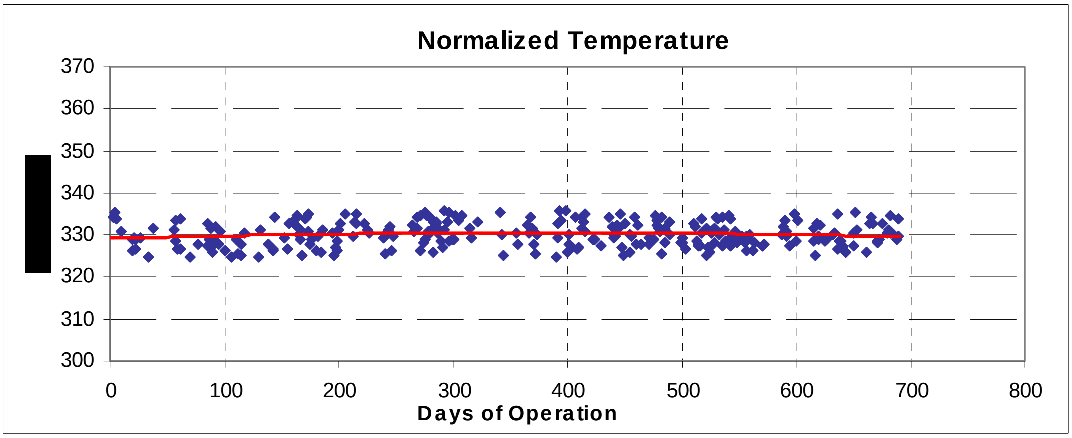
An inconvenient in deriving feed properties correlation functions is the availability of feed analysis data in day to day refinery operation. We decided that feed correlations included in our models should be based on properties commonly measured in refineries. Next figure shows the fitting of two correlations to the experimental data. The first one is based on feed sulphur, density and nitrogen, all properties readily available in refinery, and for these set of data, the best correlation we could find. The second one is based on feed DBT's (+) concentration and basic nitrogen content, properties that, in normal operation, are not available. However, the second correlation reproduces much better the experimental set of data.





As an example, next figures show the result of employing both correlations to follow up the performance of an industrial HDS unit. The good linearity of the second plot (that uses the correlation based on DBT's and basic Nitrogen) stands out against the scatter of data on the first figure. It is easy to imagine the advantages of having available second type models for this and other applications.



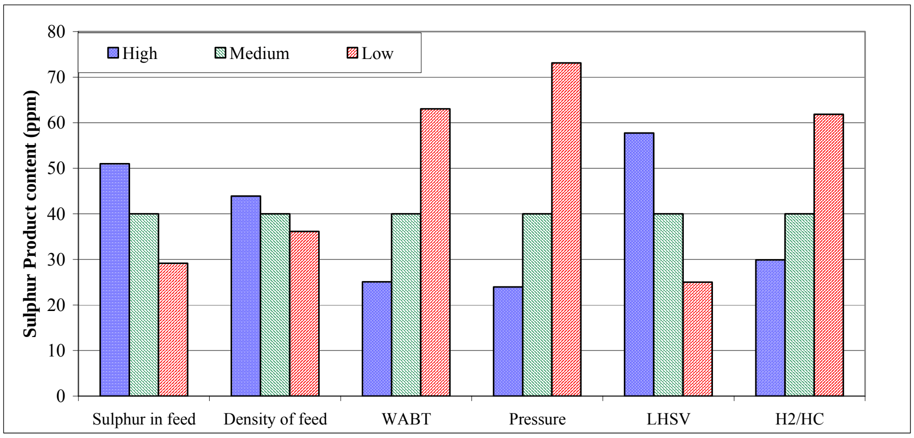


As a consequence of these and other results, new analysis routines are being implemented in our refinery laboratories that allow a better understanding of industrial unit performance.

f_4 (UNIT CALIBRATION)

A final function was included as part of the kinetic models. We understood that the scale differences between pilot and industrial units would cause deviations of model predictions versus industrial unit performance. To solve this problem in an easy manner, this new function was included as a correlation factor that adjusted model predictions to test run results carried out in most industrial units. Maximum deviations of 4 °C in terms of WABT were observed and corrected.

Finally, next figure illustrates how the model reflects the effect of some parameters commented above on the HDS activity. The development of this tool has allowed us to clearly understand the effect of these and many other parameters on the many processes taking place during hydrotratment.



For the figure above, levels high, medium and low are shown in the table:

	High	Medium	Low
Sulphur in feed (wt%)	1.5	1	0.75
Density (g/cc)	0.85	0.845	0.84
WABT (°C)	365	359	353
Total P (bar)	60	50	40
LHSV (h^{-1})	1.2	1	0.8
RHC (Nm^3/m^3)	250	200	150

3.2.- Deactivation studies for industrial HDS units

At one stage we learned that knowledge of catalyst deactivation rates in industrial units was necessary to complete our studies. From licensors and catalyst manufacturers we obtained analysis of particular study cases proposed to them, but not a general tool to study all the scenarios and cases that we required. We also understood that this information could not be obtained from pilot plant data. In consequence we decided to develop our own deactivation models based on the analysis of industrial data.

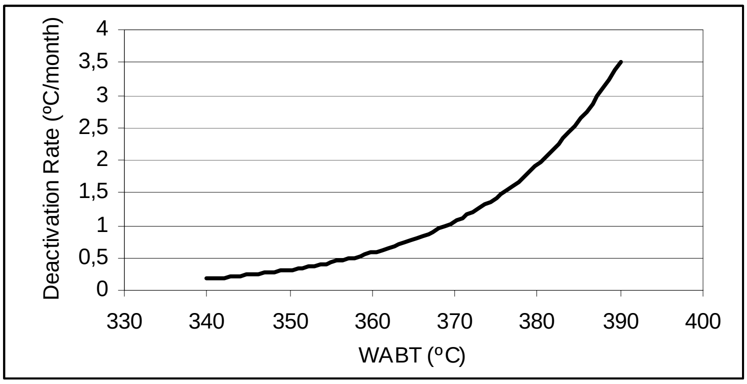
Data from all of our HDS units were collected as to assemble a set of more than 30 complete cycles. These data were analysed on the basis that deactivation depends on feed properties and operating conditions and not on sulphur concentration in the desulphurised product. The collected data fairly covered the range of feed characteristics and operating conditions expected for 50 and 10 ppm operations.

After normalisation of industrial data using the kinetic models explained above we studied the influence on deactivation rate of the available operating parameters and feed properties:

- Operating parameters: WABT, LHSV, P_{H2}, % Vaporisation
- Feed properties: Sulphur, specific gravity, D-86, feed origin (SR, conversion)

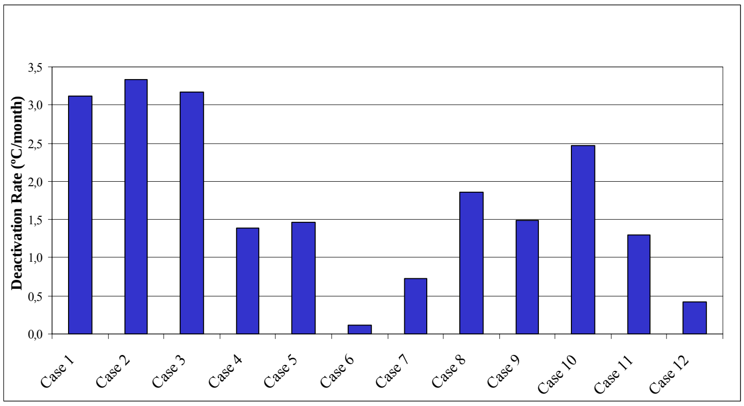
For this study, we needed to analyse a large number of industrial cycles. The analysed available data on feed properties and operating conditions did not always have enough quality. Then, our best solution was to divide industrial plants in two groups, according to the type of feed treated. For each group we derived specific models that did not contain feed properties as parameters, but only operating conditions. The following plot shows for constant space velocity and hydrogen partial pressure, our estimations for the rate of deactivation in HDS units processing straight run feeds.

Deactivation rate as a function of WABT

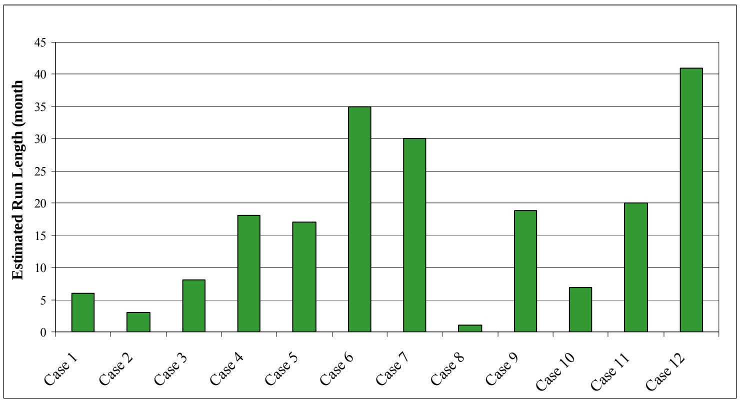


These models have been employed to estimate cycle lengths in industrial Units. Next figures show our initial estimations of deactivation rates and cycle lengths for desulphurisation to 10 ppm of sulphur without modification of industrial Units for different study cases.

Deactivation rate for industrial Units



Estimated cycle lengths



The high values of deactivation rates, and the low cycle lengths estimated were due to the elevated SOR temperatures required for continuously producing 10ppm diesel without unit revamps.

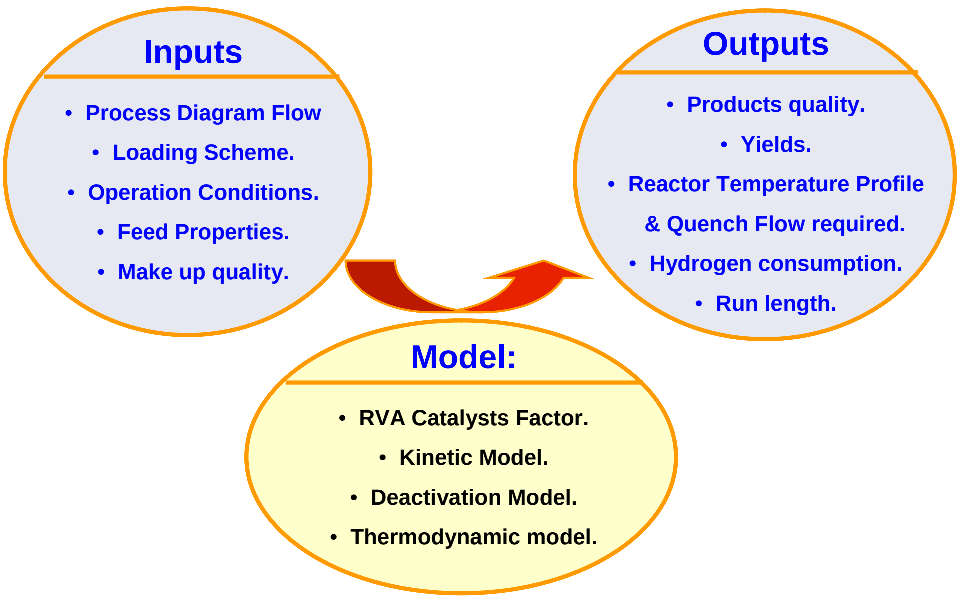
3.3.- Classification of catalysts performance

New developments and improvements in catalysts performance have been of great help for reducing extra volume requirements for HDS industrial units. Throughout our work, we classified commercial catalysts from main manufacturers in terms of its HDS, HDN, HDA pilot plant activity, and expected cycle length. So obtained activity factors were included in kinetic models as shown above. Where possible, all experimental pilot plant data were checked with industrial operations

We learned from our own data the advantages of using CoMo or NiMo catalysts, and its relationship with feed characteristics and industrial operating conditions. From these results, catalyst loading schemes for industrial units were defined.

3.4.- Development of a general HDS unit simulation model Alternativas para minimizar la contaminación de los catalizadores de la unidad de hidrotratamiento

Finally, a complete model for simulation of industrial HDS units was developed. For this, firstly our own developed kinetic and deactivation tools were included together in a single codified program. We called this program Rep_HDS. Then, Rep_HDS was linked together with a commercial thermodynamic simulation program. The result is a powerful tool that in a schematic way operates as follows:



This general model has been widely used to simulate industrial operations, helping to define revamping requirements, optimising units operation etc. Also, this model has been adapted to follow up industrial units performance.

4.- Assessment results

Different cases of study were defined based on LP modelling of the refineries in future scenarios, and considering the new projects to be implemented (new HC and MHC units starting up from 2003 to 2005). Capacity and feedstock quality were discussed and agreed with the refineries, as well as main units operating conditions (pressure level, hydrogen purity…). Once basis had been established, the following steps were followed using the tools described under 3 above:

- Unit simulation
- Kinetic evaluation (SOR WABT, deactivation rate) and cycle length estimation
- Consultations to catalyst vendors and licensors
- Test runs for specific units
- Refinery hydrogen and sulphur balances
- Study conclusions and recommendations

4.1- Scenario 1: 100% 50 ppm diesel production

Fourteen units in five refineries were studied. It was concluded that most units would be able to produce this diesel quality by a moderate increase in severity that would allow keeping cycle lengths higher than 30-36 months. Only minor modifications were defined for some units, mainly related to reliability of some equipment: replacement of old compressors, piping renewal, H2 purity improvement in some units. A reforming unit in Cartagena was also modified to improve hydrogen production.

The future projects were introducing certain flexibilities that were helping to achieve this objective:

- HC and MHC projects would leave room for middle distillates desulphurization in units being traditionally used for VGO hydrotreating in at least two of the five refineries evaluated.
- The new MHC project in a third refinery would be prepared to treat LCO, leaving room in one of the existing HDS units for other middle distillates easier to desulphurize.

Other factors in the appropriate direction were:

- CO and coker gasoil being segregated to non road gasoil and heating oil pools.
- Catalyst development: more active catalyst available in the market.

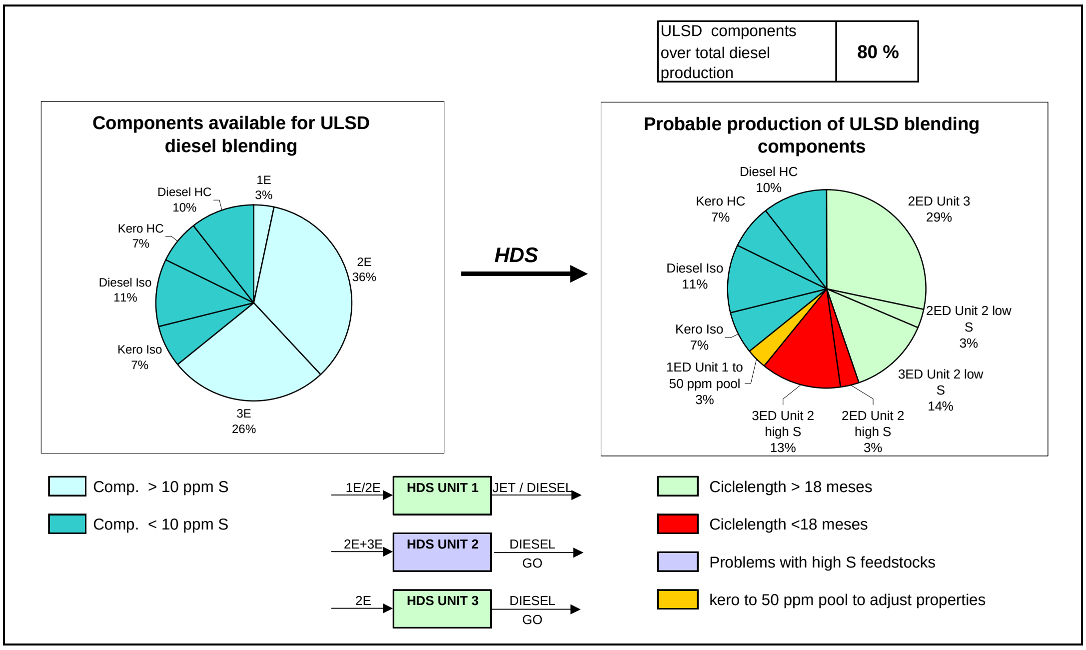
4.2.- Scenario 2: simultaneous production of 50 and 10 ppm diesel

The objective of this study was to determine the amount of 10 ppm diesel that could be produced with the units prepared for 50 ppm, without significant investment in the refineries.
ULSD production was studied from the kinetic perspective, analyzing the hydrodesulphurization capacity of the units to produce 10 ppm diesel, and also from a logistic point of view.

The following types of units were identified:

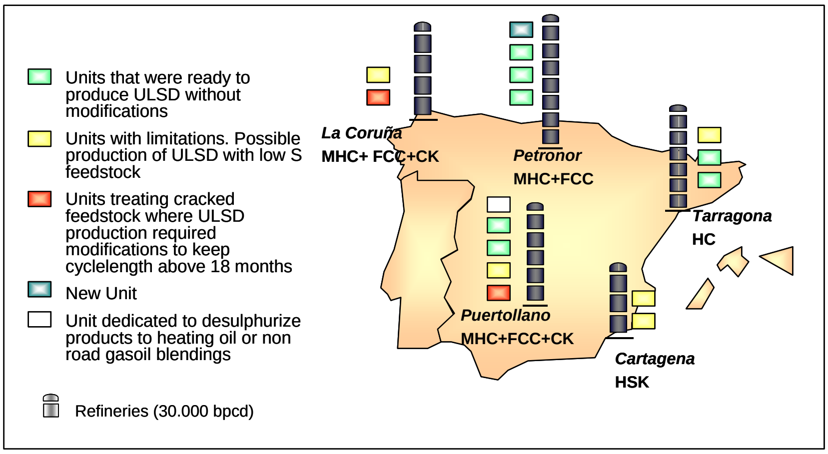
- Low pressure units (H2 partial pressure below 25 bar) that could desulphurize to 10 ppm kero and light straight run distillates (second extraction from topping column), and low sulphur mixtures of straight run distillates (mixtures of second and third extraction from topping column).
- Moderate pressure units (H2 partial pressure in the range 35-40 bar) processing mixtures of SR GO and cracked feedstock (mainly light coker gasoil) that were capable to produce 10 ppm diesel, but with a significant penalty in cycle length.
- High pressure units (H2 partial pressure above 40 bar), were it was possible to process moderate percentages of LCO (15-25%) to 10 ppm sulphur level.

Assuming 18 months as the minimum acceptable cycle length, and considering the typical crude slate of each refinery during a year, the different sulphur levels of the crude oil being processed, and the type of units in each refinery, an estimation of the percentage of the total volume of diesel that could be produced with less than 10 ppm was performed. As an example, next figure summarizes the results of the study for Tarragona refinery. According to our study, this refinery would be able to produce around 80% of the diesel pool with less than 10 ppm S and higher than 18 months cycles in the existing HDS units without modifications.



At the same time, logistic limitations to segregate different gasoil qualities were evaluated. Although production of 50 and 10 ppm simultaneously would introduce complexity in the operations, most modifications required were those to segregate the logistics of 50 ppm diesel and 2000 ppm gasoil. Next figure shows these results:

RepsolYPF HDS units in Spain: ULSD Evaluation (2002)



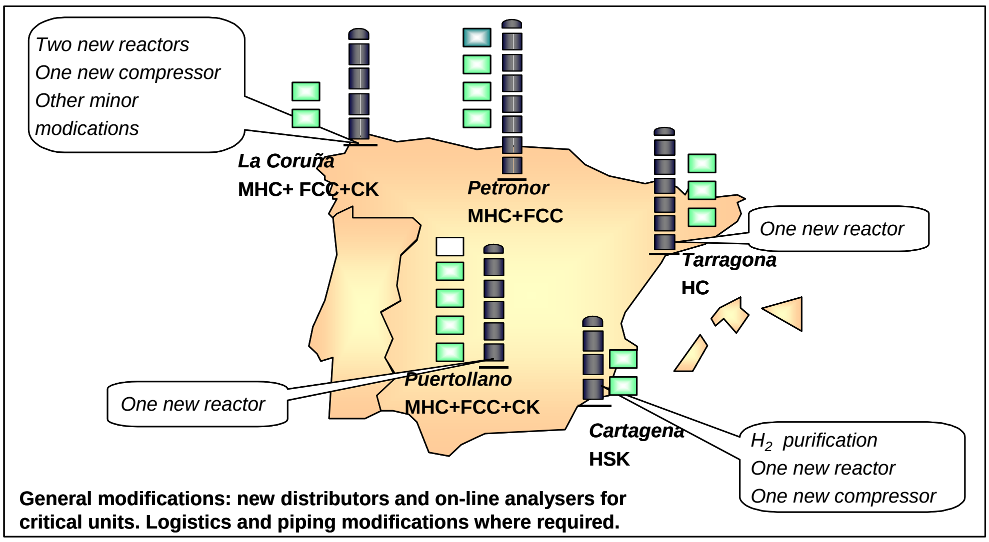
4.-3 New projects for 100% 10 ppm diesel production Bibliografía

As a result of the exercise previously described, the need to implement modifications in some of the existing units in order to achieve the complete production of ULSD was identified. In order to improve performance, the following measures were considered:

- Use of high activity catalysts.
- Dense loading.
- Feedstock segregation (when possible).
- Installation of high performance distributor trays in critical units.
- Installation of online sulphur analysers for diesel product.
- Hydrogen purity improvement when possible.
- Reducing space velocity (new reactor in series to existing).

Engineering definition of the projects for those units requiring changes were launched in 2003. The preliminary engineering work required for investment estimation and project approval was performed internally. These projects are now at different stages of engineering and construction.

2003 Project definition



5.- Conclusions

For the last few years RepsolYPF has been working to adapt the Spanish refineries to the production of ULSD fuel. This work has been carried out in several stages described in this paper. As a final outcome, a number of modifications affecting the production units and the logistic infrastructure were approved. These projects, that will allow us to produce 100% of our diesel auto with less than 10 ppm of sulphur, are now at different levels of implementation.

As an intermediate step, the capacity of the refineries to produce simultaneously 50 and 10 ppm diesel was evaluated. In this study, the availability for producing ULSD for each refinery was found to be different. In consequence, a detailed picture of production capacities was elaborated. At present time, these capacities are being extensively used, and important quantities of 10 ppm diesel are being produced.

To support this work, an important R&D effort was launched at our Technology Division. This effort crystallised in the development of several tools, including a simulation model fully validated for our industrial units.

A final remark. Throughout this work, a large amount of knowledge has been achieved within our Company. Some of this knowledge has been developed internally, and some has been acquired by consultations to others. In any case, we think that the result has deserved the effort, and we are now in a much better position to understand the HDT processes, and hence to obtain the best performance from our industrial plants.