TITLE: THE ROLE OF R&D IN IMPROVING REFINING AND PETROCHEMICAL COMPANIES' RESILIENCE AGAINST MARKET VOLATILITY AND CHANGES IN LEGISLATION BY PROPER KNOWLEDGE MANAGEMENT

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ABSTRACT:

Nowadays, the refining-petrochemical companies have to maximize the practical valorization of their knowledge in order to develop competitive advantages facing the sudden changes of exogenous factors: raw materials pricing, development of new catalysts and changes on specifications from new products and/or new legislations.

Regarding the practical valorization of their know-how, it should be pointed out the strategic need of optimizing the efficiency of their catalytic processes by:

a) Developing predictable process models based on integrating information from industrial plant and laboratory pilot plant

b) Use the information of the validated models to select the best combination of catalysts and crude oil basket

In this article, it will be presented an example about how the changes in exogenous factors (expressed by changes in legislation of fuels, such as changes in terms of sulphur specification and the introduction of new opportunity crudes in the refinery) can be confronted through and adequate knowledge management system. By properly managing knowledge (industrial data and research results), an economically valuable tool can provide a relevant competitive advantage.

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A brief overview of exogenous factors

The historical trends in the refining industry show that raw materials pricing face quite volatile environment because of supply-demand issues (weak economics, geopolitical conflicts, etc.). On the other hand, changes on legislation regarding fuel environmental issues push refining companies to be able to adapt their process systems according to the new specifications in the more flexible and profitable way. Appropriate selection of raw materials (crude oil basket) and catalysts is a duty for these companies in order to get adapted to this changing scenario.

Regarding raw materials, we can find different crudes from different origins, such as Maya from Mexico, Arabian Light from Abu Dhabi, Kirkuk from Irak, among others. In Table 1 is showed an example of three crudes with the main properties.

Table 1. Crude assay summary report. Source: Spiral Crude Suite

Crude			Maya	Arabian Light	Kirkuk
Density 15ºC (g/cm^3)			0,920	0,858	0,849
API Gravity			22,2	33,4	35,1
Total Sulphur (% wt)			3,3	1,77	2,0
Yields (%wt) Atmospheric Cuts	Start (°C)	End (°C)			
	C5	65	1,9	3,4	3,9
	65	100	2,9	3,8	4,9
	100	150	4,8	7,4	8,3
	150	200	5,7	9,0	9,6
	200	250	6,0	9,0	10,2
	250	300	6,7	9,0	7,1
	300	350	6,9	8,6	7,6
	350	370	2,6	3,4	4,5
	370	FBP	62,5	45,4	42,0
Yields (%wt) Vacuum Cuts	370	450	9,0	12,6	12,3
	450	500	5,1	7,0	7,2
	500	550	5,3	6,2	6,3
	550	FBP	43,2	19,6	16,2

The crudes differ among themselves based on the direct yields to the different cuts (gases, naphtha, kerosene, diesel, vacuum gas oil), API Gravity, etcetera. The higher the API Gravity, the lighter the crude. The different products have more or less economic value depending on the market situation. Besides that, each crude contains different chemical compounds that could be poisons for downstream units (different metal content, sulphur and nitrogen). For this reason, the definition of the crude oil basket for a refinery is of great importance.

There are some reference crudes that act as a benchmark on pricing: Brent crude for Europe, West Texas Intermediate for United Stated and America and Dubai for Middle East. However, nowadays it is common to acquire and process crudes named "opportunity crudes" because of their significantly lower price. The main difference when compared to the reference ones is that these crudes are cheaper but some of them are heavier crudes (lower yield to middle distillates, which are more demanded) and also contains more poisons than the reference ones.

The presence of certain compounds such as nitrogen and sulphur in final products has negative impact in terms of environment and air pollution. In case of nitrogen, the combustion of fuels produces nitrogen oxides and in case of sulphur, it produces sulphur oxides. Both compounds are harmful for the environment and their content in fuels are strictly regulated by law.

Due to legislation, the sulphur content in fuels is day by day more limited. The European Union, based on the European Committee for Standarization has developed several standards along the years. As it is showed in Figure 1, before 1996, the Diesel contained 2000 parts per million by weight (ppmwt). From 1996 to 1999 it was limited to 500 ppmwt, from 1999 to 2004 the maximum allowance was 350 ppmwt, from 2004-2009 the specification changed to 50 ppm wt and from 2009 the current specification is 10 ppm wt.

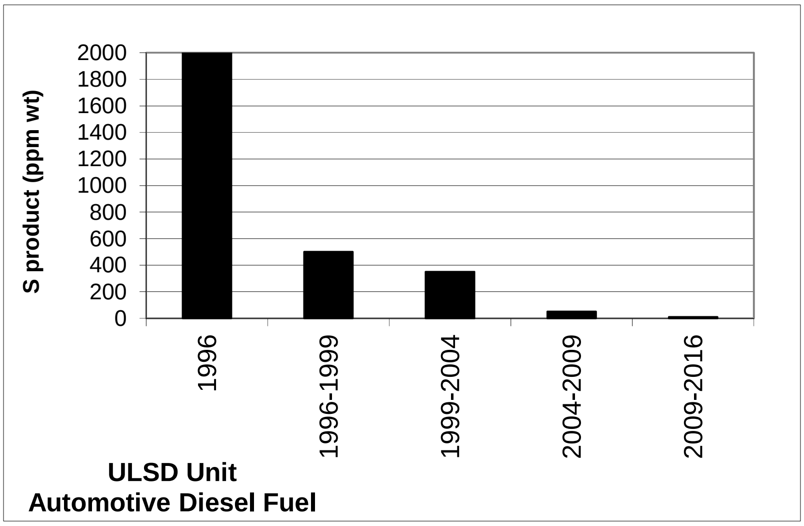

Figure 1. Sulphur limits. Source: Ministry of Agriculture, Food and Environment of Spain

All these changes in legislation have forced refineries to optimize their crude oil basket while increasing the severity of hydrotreatment and conversion processes. At the same time, catalyst suppliers have improved their catalyst's design by the years and also the refinery has changed the operations in the industrial units.

How to face the challenge through knowledge management?

From the point of view of a refinery, based on the need of producingfuels such as diesel with lower and lower sulfur contents because of the more severe legislation, the refining companies can play with different options:

1) Purchase crudes that only require distillation in order to getrequired diesel output under specification. Only one step would be needed and it wouldn't be necessary a catalytic process.Unfortunately, crudes that may allow this solution are too expensive.

2) Purchase crudes that require distillation in order to get required amount of diesel but its sulphur content would be above specification. In order to achieve the sulphur specification a hydrotreatment (hydrodesulphurization) process is required.

3) Purchase crudes with low direct diesel yields (it will be required a conversion process to convert heavy fraction into diesel) that are cheaper than previous ones. By processing crudes with technologies such as fluid catalytic cracking followed by a hydrotreatment step or hydrocracking in presence of hydrogen, diesel output under required sulfur specifications is possible. However, these cheaper crudes require anupstream hydrotreatment step in order to eliminate those substances that poison the catalysts used in conversion steps. At this stage the refinery need to select the catalyst and operating conditions in order to get the final product at a profitable yield.

Within these three possibilities the most common are the second and third one. In both cases, a hydrotreatment process is required.

Taking into account that there are so many combinations for producing diesel with certain sulfur content (different crudes, different processes and different catalysts), research and development (R&D) departments have to play an important role in order to optimize the combination of these factors to get the best hydrotreatment system.

If we talk about hydrotreatment units, specifically the Ultra-Low Sulphur Diesel (ULSD) ones, these units can process different feedstock (Straight Run Gas Oil from crude oil distillation step, Light Cycle Oil from Fluid Catalytic Cracking unit, Visbreaking Gas Oil from Visbreaking unit, etcetera) and it is necessary the presence of hydrogen (from Reforming or Steam Reforming Units). These units eliminate certain undesired heteroatoms (sulphur, nitrogen, metals); allowing to comply with the legislation while removing poisons for downstream units, such as the petrochemical units.

The heart of this kind of processes is the catalyst. It is well known that hydrotreatment catalystsare characterized by three main parameters: activity (degree of desulphurization / denitrification /demetallization achievable for a certain raw material and operating conditions), stability (resistance to deactivation caused by poisoning / soiling) and life (duration of cycle before requiring uneconomic operating conditions to maintain a certain activity degree). In the past, catalysts' developments were based on basic trial-and-error experimentation. Nowadays, the development of new high throughput catalyst production (robotized catalyst samples preparation) and ultrafast testing procedures (high throughput reactors), in combination with neural networks that correlates changes in the catalyst composition with changes in their activity, has fastened the development of new catalysts. The catalysts for ULSD units are typically based on nickel-molybdenum or cobalt-molybdenum supported on alumina. They belong to the group of bulk, or non-porous catalysts, as all the active phase (metals) are located on the external surface of the support.

As a logical issue, it is necessary for the refinery to optimize the economy of their catalytic processes, which implies optimizing the combination of raw material, catalyst type and operating conditions in order to minimize Operating Costs (OPEX) such as energy, hydrogen or catalyst, among others.

The whole cycle for developing and implementing a new catalyst comprises the steps summarized in the following diagram (Figure 2):

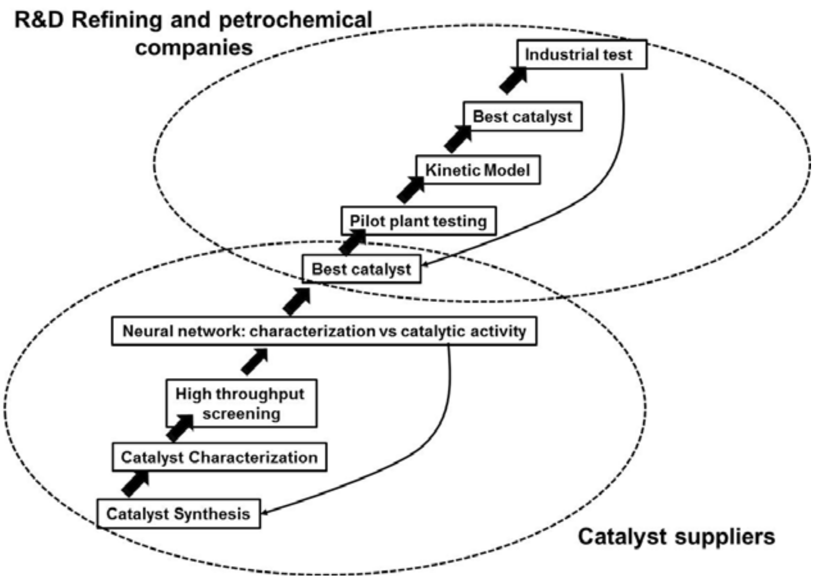

Figure 2. Catalyst development cycle. Source: Prepared by the author

From the point of view of a refining and petrochemical company, which normally doesn´t develop their own catalysts as this is not the core of their business, the support of R&D departments usually starts asking catalyst producers for providing appropriate catalyst samples. After that, it is necessary to develop an experimental design at pilot plant scale in order to determine which of the different catalysts provided by different suppliers better fits the requirements of the industrial plant where it will be charged.

In order to develop a robust experimental design, it is very important to define a representative feedstock from the crude oil basket that contains all the main undesired compounds that in the real situation the unit would have to process. The more different feeds are used, the more robust model will be developed.

As hydrotreatment catalyst have no micro-porous and therefore all the active phase is located on the surface, theoretical models based on adsorption of the reactants (hydrogen, sulphur, nitrogen compound) on active site, reaction step and desorption of the products are used. The more common models are isothermal adsorption ones, such as Langmuir-Hinshelwood or related ones. By adjusting these theoretical models with the experimental data (desulphurization, denitrification rates) obtained from pilot plant at steady state, it can be determined which of them better fits. To do so, it´s necessary to evaluate the error between the experimental reaction rate and the calculated one (reaction rate calculated with model). It is also necessary to recalculate models along catalyst cycle in order to determine the deactivation rate of each catalyst, which is then coupled to the initial activity kinetic model. Once we have the micro-kinetic model including deactivation rates for all available catalysts, it is necessary to couple them with the characteristics of the industrial reactor (fixed bed, adiabatic reactor, catalyst particle size, reactor length and diameter), in order to achieve the final macro-kinetic model.

Selection of the best catalyst is achieved by applying macro-kinetic models to calculate global hydrodesulphurization rates under the defined ranges of industrial conditions (temperature, hydrogen partial pressure, sulfur-nitrogen concentration, flow rate, etcetera). The catalyst that provides higher reaction rates (desulphurization) at the most economical operating conditions (lower temperature, lower hydrogen partial pressure, higher flow rates, higher cycle length) can be considered as the best one from a technical point of view.

On the other hand, in order to select the best catalyst, it is important to take into account other relevant aspects as: catalyst price, possibility of being regenerated after its cycle life and behavior of the regenerated catalyst, mechanical resistance (important for avoiding catalyst degradation during loading procedure), etcetera.

But the support of R&D doesn't ends at this point. Once the selected catalyst is loaded in the industrial unit, indeed starts an even more important support. R&D people in combination with process engineers have to follow-up the catalyst performance during the cycle in order to check the deviations versus the kinetic model based predictions. Deviations from the model can be related to fluid-dynamic problems (by-pass, channeling, etc) or unexpected chemical deactivation.

Fluid-dynamic problems can be confirmed by analyzing the normalized delta pressure (pressure drop along the reactor divided by flow). If it happens, it is important to determine the origin in order to find a solution. To do so, the most habitual procedure from R&D is analyzing the characteristics of the particles retained at the filters located upstream, which most probably are also the cause of the problem in the downstream reactor. If filter plugging is caused by metal particles coming from upstream corrosion problems, the solution has two levels. On one hand, it has to be defined the exact origin of the particles in order to help the engineers to find the origin of the problem. A complete knowledge of the chemical composition of the upstream's metallurgy and availability of the appropriate analysis' techniques is crucial. On the other hand, if filter plugging is caused by chemical substances present in the raw material (e.g.: polymers) the source has to be studied in order to define if it is economically feasible to remove them (specific filters, degumming process, etcetera) or if it is better to change the raw material which indeed affects the selection of the crude oil basket. In many cases asphaltenes are responsible of this kind of plugging.

If deviation is related to chemical deactivation, it is important to check the presence of impurities not included in the raw material that was used at pilot plant level. To do so, it is important to get representative samples from the industrial raw material and submit them to a battery of chemical analyses. This would help to determine the presence of poisons that were not present in the feedstock used at pilot plant tests, which are related to changes on the reference crude oil basket. Knowing the impact of these unevaluated poisons in catalyst activity, it allows to a better economically characterization of the industrially used crude oil basket.

Deviations founded versus model are not only useful for finding solutions for the industrial plant issues, but also are quite important to be retrofitted to pilot plant experimental design in order to get a continuous improvement in the accuracy of the models or even on the selection of the best catalyst. It may occur that when re-testing all the catalysts provided by suppliers with the feedstock that created industrial problems, the best catalyst might change. At this point it would be necessary to determine if, from an economically point of view, it would be better to change the catalyst or the feedstock (and therefore, the crude oil basket).

Conclusions

The appropriate management of the combined knowledge from R&D kinetic models and industrial data, allows refining and petrochemical companies to get competitive advantages. By developing a feedback feed-forward knowledge cycle as summarized in Figure 3, the decision of which crude's basket and which catalyst system (catalyst and operating conditions) are the best for solving changes in the exogenous factors can be better made. Therefore, industry can face volatility on raw materials prices and changes on legislation in the most effective way.

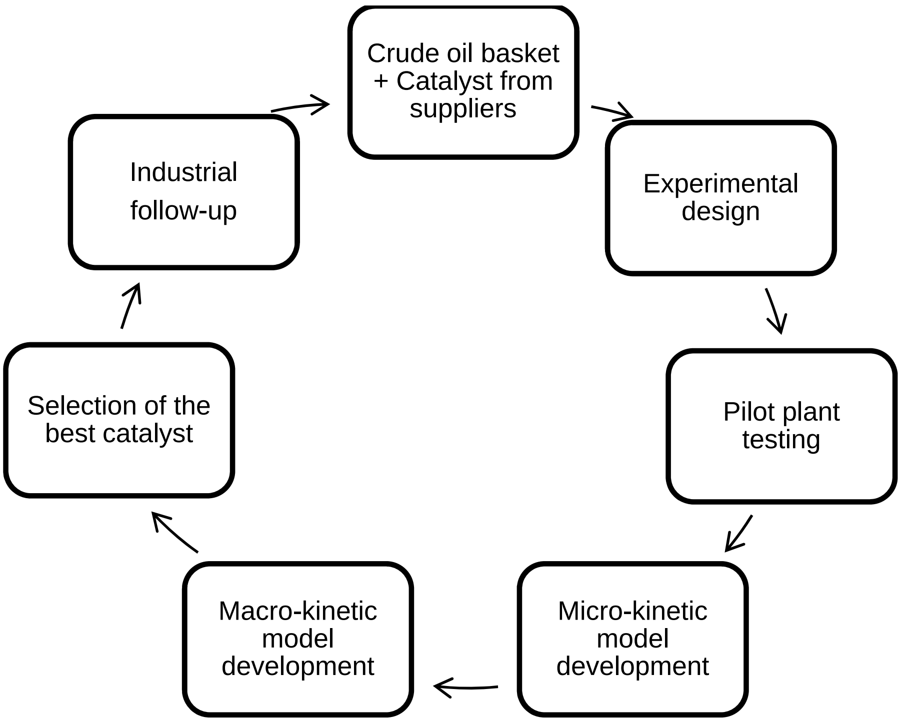

Figure 3. Knowledge management cycle. Source: Prepared by the author